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THE CRYSTAL STRUCTURE AND HYDROGEN BONDING OF MAGNESIUM SULFATE HEXAHYDRATE

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THE CRYSTAL STRUCTURE AND HYDROGEN BONDING OF MAGNESIUM SULFATE HEXAHYDRATE

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The Crystal Structure and Hydrogen Bonding of Magnesium Sulfate Hexahydrate*

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Crystals of $MgSO_4.6H_2O$ are monoclinic, space group C2/c, with 8 formula units in the unit cell with dimensions

$$a = 10.110,\ b = 7.212,\ c = 24.41\ \text{Å};\quad \beta = 98.30^{\circ}.$$

The atomic parameters were refined by least squares using x-ray counter data for 2576 independent reflections. The positions of the hydrogen atoms found by least squares and by Fourier methods confirm the assignment of hydrogen bonds made previously for the isomorphous $CoSO_4.6H_2O$. Average interatomic distances are: water coordinated to Mg, Mg-O = 2.06 Å; hydrogen bonds, O-O = 2.82 Å; sulfate ion, S-O = 1.473 Å (uncorrected), 1.486 Å (corrected for thermal motion).

*Work done under the auspices of the U. S. Atomic Energy Commission.

Introduction

The crystal structure of $CoSO_4.6H_2O$ has been described in a previous paper (Zalkin, Ruben, and Templeton, 1962). Hydrogen bonds were assigned on the basis of the positions of the heavier atoms, but the x-ray diffraction data did not give direct evidence of the hydrogen atom positions. The present paper describes a study of the isomorphous substance $MgSO_4.6H_2O$ for which we have obtained more accurate diffraction data. These better data permit a more accurate description of the structure and indicate hydrogen atom positions in agreement with those deduced in the earlier work.

Crystals of $MgSO_4.6H_2O$ are known in nature as the mineral hexahydrite (Dana and Ford, 1948). Other substances which have the same structure are $MgSeO_4.6H_2O$, $NiSO_4.6H_2O$, $CoSeO_4.6H_2O$, and $ZnSO_4.6H_2O$ (Groth, 1908).

Experimental

Crystals of $MgSO_4.6H_2O$ were grown from saturated aqueous solution at 50 - 55°C. Once grown and separated from the mother liquor, the exposed crystals could be kept at room temperatures for several months with no visible deterioration. A small single crystal with diameter of the order of 0.02–0.08 mm was mounted on a glass fiber and oriented for rotation about its b axis with the use of a Weissenberg camera. It was then transferred to a goniostat mounted on a General Electric XRD-5 apparatus, which was equipped with a molybdenum x-ray tube, a scintillation counter, and a pulse-height discriminator, for further alignment and data taking. Cell dimensions and crystal settings were calculated with $\lambda(K\alpha_1) = 0.70929$ Å. Intensities were measured for 2,576 reflections of which 289 were recorded

as zero. All of the reciprocal lattice points with positive h and k, out to a limit of $\sin\theta/\lambda = 0.705$ ($2\theta = 60^{\circ}$) were measured. Step scanning of the angle θ was done for selected reflections to verify the settings for peak intensity. For the typical reflection, a single count was made for a fixed time of 20 seconds.

The absorption coefficient μ for this crystal with Mo Kα x-rays is estimated as 5.0 cm^{-1}. The resulting μR is less than 0.02. No correction was made for absorption or extinction.

An accurate trial structure was provided by the structure of $CoSO_4.6H_2O$ (Zalkin, Ruben and Templeton, 1961); corresponding coordinates for atoms other than hydrogen differ by 0.01 or less in the two structures. Least-squares refinements were started using the programs of Busing and Levy (1959) on the IBM 704 computer. We then used the IBM 709 computer with the programs of Gantzel, Sparks, and Trueblood (1961). Each program utilizes the full matrix, and each minimizes the function $\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2$, where w is the weighting factor and F_o and F_c are the observed and calculated structure factors. In this calculation, each independent reflection was assigned unit weight. The atomic scattering factors used in the refinements were Mg^{++} and neutral S (Tomiie and Stam, 1958), neutral O (Hoerni and Ibers, 1954), and neutral H (Ibers, 1961).

Space Group and Cell Dimensions

The space group is C2/c (C_{2h}^6). Reflections are absent with h+k odd, and $h0\ell$ reflections are absent with ℓ odd. The cell dimensions are:

$a = 10.110 \pm 0.005$, $b = 7.212 \pm 0.004$, $c = 24.41 \pm 0.01$ Å
(10.06) (7.16) (24.39)
$\beta = 98.30 \pm 0.05^\circ$ $Z = 8$ $V = 1761.2$ Å^3.
(98.57)

The values in parentheses are those reported by Ide (1938), changed from kX. The calculated x-ray density is 1.723 g/cm^3. The a:b:c ratios found in this and in previous work are:

1.402 : 1 : 3.384, $\beta = 98.30^\circ$ (this work),
1.404 : 1 : 3.404, $\beta = 98.57^\circ$ (Ide, 1938),
1.404 : 1 : 3.337, $\beta = 98.57^\circ$ (Marignac, 1855).

The eight Mg atoms occupy two sets of positions 4(a) and 4(e) (notation of International Tables, 1952):

4(a): (0, 0, 0; 0, 0, 1/2) + C centering,
4(e): (0, y, 1/4; 0, -y, 3/4) + C centering.

The sulfur atoms, ten sets of oxygen atoms, and twelve sets of hydrogen atoms occupy general positions:

8(f): $\pm(x, y, z;\ -x, y, \frac{1}{2} - z)$ + C centering.

Refinement Procedure

At first hydrogen was omitted from the calculations. With isotropic temperature factors of the form $\exp(-B\sin^2\theta/\lambda^2)$ for each atom, $R = \sum||F_o|-|F_c||/\sum|F_o|$ was reduced to 0.120 by three cycles of least squares. After correction of a few blunders in the original measurements, two more cycles reduced R to 0.118.

A three-dimensional Fourier synthesis with (F_o-F_c) as coefficients was calculated to seek out the hydrogen atoms. The resulting maps showed a peak wherever a hydrogen atom was expected, as well as many others of

about the same size which resulted from the anisotropic motion of oxygen atoms. A final isotropic refinement which included the hydrogen atoms but did not refine them resulted in R = 0.115.

Anisotropic temperature factors of the form $\exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}\ell^2 - 2\beta_{12}hk - 2\beta_{13}h\ell - 2\beta_{23}k\ell)$ were introduced for Mg, S and O. Three cycles with hydrogen atoms included but not refined gave R = 0.056.

A set of $(F_o - F_c)$ values were calculated with the resulting parameters for Mg, S, and O, but omitting hydrogen. Another "difference Fourier" was calculated using these numbers as coefficients. The twelve largest peaks in this function (Fig. 1) were near the predicted locations of the twelve hydrogen atoms.

As our least-squares programs at this time could not handle at one time a refinement of all the atoms including hydrogen with all the anisotropic thermal parameters, we ran a series of calculations refining parts of the structure separately. Temperature factors were isotropic for H and anisotropic for the other atoms. First the H atoms were included but not refined, while all other parameters were refined. Next H atoms were refined with the other atoms fixed. Then Mg atoms were held fixed while all other atoms were refined; in this series only the 923 reflections with $\sin\theta/\lambda$ less than 0.5 were included. Finally the H atoms were fixed and all other atoms were refined. All this calculation reduced R to 0.053 for the 2576 reflections, including those with zero intensity. In the final cycle no coordinate or thermal parameter shifted more than 0.000001.

The resulting observed and calculated structure factors are shown in Table 1. The corresponding coordinates are listed in Table 2 and the thermal parameters in Tables 3 and 4.

By a special patch, the program was modified to allow simultaneous

refinement of all 159 variable parameters. Two cycles yielded no significant improvement in R nor any substantial change in coordinates. The results are not reported because parameters were oscillating; further cycles to attain convergence (at 0.9 hours per cycle with IBM 7090) seemed unjustified.

Standard deviations of coordinates estimated by least squares, with neglect of the possible error in the hydrogen parameters, are reported in Table 2. The similar estimates of standard deviations of the anisotropic thermal parameters range from 2 to 4 percent of the diagonal elements of the β matrices. They are not reported in detail because the effects of systematic errors in the data and of coupling with hydrogen parameters are of unknown and possibly considerably larger magnitude.

The standard deviations of hydrogen coordinates correspond to about 0.05 Å when estimated by least squares with neglect of errors in heavy atom parameters. The least-squares results and the Fourier results (Fig. 1) disagree in several cases by about 0.1 Å. The best evidence of the accuracy of these coordinates comes from the O-H hond distances which are expected to be somewhere in the range 0.9 to 1.0 Å, depending on the magnitude of the thermal motion effect. We find values 0.7 to 1.1 Å for eleven such bonds and 0.5 Å for O(7)-H(6). This scatter suggests 0.2 Å as the standard deviation of position of hydrogen, including the effects of systematic errors in the data.

The standard deviations of isotropic thermal parameters of hydrogen are estimated by least squares to range from 0.7 $Å^2$ for H(11) to 1.5 $Å^2$ for H(6). The scatter from the average value of 3.4 $Å^2$ corresponds to $\sigma = 1.8$ $Å^2$. This latter value may be a better estimate of the true accuracy, since there is no obvious reason for the thermal motions of the various hydrogen atoms to be substantially different.

Discussion

The structure of $MgSO_4.6H_2O$ differs very slightly from that already described for $CoSO_4.6H_2O$ (Zalkin, Ruben and Templeton, 1962). The hydrogen bonds which were assigned in the previous study on the basis of oxygen positions are fully confirmed by the present results.

Table 5 lists some interatomic distances and their standard deviations, with no correction for thermal motion. The S-O bond distances in the sulfate ion average 1.473 Å with an average deviation of 0.007 Å. When a librational correction is made assuming the oxygen atoms to ride on the sulfur atom, the average becomes 1.486 Å with an average deviation of 0.004 Å. In the Tutton salt $Mg(NH_4)_2(SO_4)_2.6H_2O$ Margulis and Templeton (1962) also found 1.486 Å for the average S-O distance when it was corrected in the same way.

The average Mg-O distance is 2.06 Å without correction for thermal motion. Magnesium is also in water octahedra in $Mg(NH_4)_2(SO_4)_2.6H_2O$ with average Mg-O = 2.07 Å and in $Ce_2Mg_3(NO_3)_{12}.24H_2O$ (Templeton, Zalkin and Forrester, 1962) with average Mg-O = 2.06 Å. In all three crystals the average Mg-O distance is 2.07 Å with thermal correction assuming in-phase motion.

The hydrogen bond O-O distances average 2.82 Å, but scatter over a considerable range as is common in complicated hydrate structures. The accuracy of the hydrogen positions, about 0.2 Å, does not justify tabulation of the many bond distances and angles involving hydrogen atoms.

References

BUSING, W. R. and LEVY, H. A. (1959). Oak Ridge National Laboratory Report 59-4-37.

DANA, E. S. and FORD, W. E. (1948). A Textbook of Mineralogy, 763. New York: Wiley.

GANTZEL, P. K., SPARKS, R. A. and TRUEBLOOD, K. N. (1961). Private communication.

GROTH, P. (1908). Chemische Krystallographie, v. 2, 422. Leipzig: Engelmann.

HOERNI, J. I. and IBERS, J. A. (1954). Acta Cryst. 7, 744.

IBERS, J. A. (1962). International Tables for X-ray Crystallography, v. 3, 202. Birmingham: Kynoch.

IDE, K. H. (1938). Naturwiss. 26, 411.

International Tables for X-ray Crystallography (1952), v. 1, 101. Birmingham: Kynoch.

MARGULIS, T. N. and TEMPLETON, D. H. (1962). Z. Krist. 117, 344.

MARIGNAC, CH. DE (1855). Arch. sc. phys. et nat. Geneve, (1), 14, 234 (quoted by Groth, 1908).

TEMPLETON, D. H., ZALKIN, A. and FORRESTER, J. D. (1962). Bull. Am. Phys. Soc. 7, 608.

TOMIIE, Y. and STAM, C. H. (1958). Acta Cryst. 11, 126.

ZALKIN, A., RUBEN, H. and TEMPLETON, D. H. (1962). Acta Cryst. 15, 1219.

Table 1. Observed and calculated structure factors, each multiplied by 10.

(table to be reproduced photographically in two parts)

```
H,K= 0, 0
 L FOBS FCAL
 2  50  42
 4  453 -459
 6  73  62
 8  525 513
10  597 -582
12  710 -724
14  480 423
16  1161 1159
18  468 495
20  657 -671
22  0  -27
24  522 540
26  146 -174
28  0  42
30  121 -107
32  340 338

H,K= 2, 0
 L FOBS FCAL
32  0  46
30  102 -117
28  119 131
26  229 231
24  0  7
22  479 -464
20  401 397
18  1492 1519
16  368 370
14  326 -339
12  1930 1964
10  436 -435
8  46  40
6  2511-2634
4  1447 1436
2  1574 1560
0  903 822
-2  1620-1637
-4  1255 1218
-6  1513 1552
-8  2195-2256

H,K=10, 0
 L FOBS FCAL
-10  383 -362
-12  323 292
-14  674 693
-16  140 151
-18  672 -657
-20  645 655
-22  190 205
-24  505 512
-26  206 -208
-28  304 333
-30  193 176
-32  184 158
-34  187 -191

H,K= 4, 0
 L FOBS FCAL
30  256 278
28  180 186
26  105 -92
24  119 -135
22  0  -29
20  683 699
18  416 -408
16  140 144
14  409 396
12  1197 1182
10  1312-1289

H,K=12, 0
 L FOBS FCAL
8  199 216
6  221 208
4  73  28
2  683 -668
0  736 -741
-2  1841 1853
-4  662 687
-6  832 813
-8  1000 979
-10  616 598
-12  1284 1303
-14  571 -541
-16  188 186
-18  156 -200
-20  863 854
-22  203 -194
-24  157 164
-26  0  9
-28  257 253
-30  81  72
-32  204 -190
-34  0  1

H,K= 6, 0
 L FOBS FCAL
28  0  16
26  111 -128
24  339 331
22  77  -65
20  9  9
18  479 -466
16  473 471
14  204 176
12  537 543
10  549 569
8  638 635
6  953 944
4  294 -245
2  227 -234
0  434 447
-2  36  49
-4  650 641
-6  230 209
-8  883 885
-10  351 -340
-12  729 749
-14  1054-1057

-16  275 268
-18  394 346
-20  34  49
-22  208 -185
-24  82  95
-26  224 218
-28  0  -5
-30  157 -123
-32  123 122

H,K= 8, 0
 L FOBS FCAL
24  422 458
22  84  -87
20  121 -112
18  55  77
16  124 92
14  108 103
12  206 196
10  259 249
8  632 608
6  240 269
4  498 -490
2  466 -484
0  872 879
-2  635 -634
-4  377 370
-6  218 -210
-8  667 630
-10  146 -144
-12  120 -136
-14  123 116
-16  682 706
-18  293 296
-20  131 -140
-22  274 267
-24  244 247
-26  135 -133
-28  42  -37
-30  0  29

H,K=10, 0
 L FOBS FCAL
20  88  105
18  225 244
16  226 -239
14  237 -251
12  244 236
10  201 163
8  344 342
6  511 -522
4  405 403
2  436 444
0  446 420
-2  419 -409
-4  610 608
-6  451 454
-8  70  -86
-10  238 -190
-12  176 177
-14  510 511
-16  0  50
-18  86 -121
-20  256 259
-22  41  43
-24  0  8
-26  241 -243

H,K=12, 0
 L FOBS FCAL
14  147 159
12  407 423
10  244 -281
8  0  13
6  200 174
4  497 516
2  98  -97
0  158 -120
-2  286 304
-4  245 252
-6  142 -138
-8  295 -268
-10  143 151
-12  284 273
-14  223 -209
-16  0  -14
-18  42  -1
-20  212 259
-22  140 -150

H,K=14, 0
 L FOBS FCAL
0  193 182
-2  88  107
-4  44  -78
-6  62  -66
-8  285 298
-10  99  125

H,K= 1, 1
 L FOBS FCAL
33  88  96
32  61  -41
31  59  64
30  41  25
29  98  -71
28  368 343
27  239 -230
26  296 -296
25  63  35
24  35  -44
23  0  2
22  455 463
21  203 -187
20  524 519
19  118 -100

18  325 -324
17  432 434
16  68  -57
15  243 233
14  659 641
13  56  -54
12 1348 1396
11  502 -511
10  333 -299
9  313 326
8  707 667
7  54  -71
6 1285 1292
5  94 -106
4 1712 1734
3  586 -563
2 1280-1254
1  358 342
0  169 128
-1  426 391
-2 1246 1249
-3  380 385
-4 2056 2252
-5  815 -793
-6 1142-1162
-7  404 384
-8  416 -431
-9 1088 1089
-10  896 898
-11  385 370
-12  269 -225
-13  296 -274
-14  907 -909
-15  83  -78
-16  225 227
-17  0  6
-18  209 189
-19  30  -41
-20  640 649
-21  443 -448
-22  157 -115
-23  112 -125
-24  35  -43
-25  228 229
-26  132 130
-27  155 143
-28  351 341
-29  163 -132
-30  210 -208
-31  59  50
-32  104 104
-33  61  55
-34  108 111

H,K= 3, 1
 L FOBS FCAL
32  213 224
31  43  -12
30  159 155
29  42  37
28  41  -51
27  40  29
26  39  -7
25  0  -20
24 570 566
23  233 -225
22  182 200
21  34  -6
20  66 -128
19  0  24
18 300 -305
17  233 235
16  961 946
15  50  -38
14 549 562
13  101 114

H,K= 7, 1
 L FOBS FCAL
12  98  -85
11  206 179
10  193 -211
9  384 374
8 1672 1665
7  427 -410
6 1352-1308
5  234 219
4 1073-1062
3  375 373
2  366 -376
1  92  87
0  352 326
-1  433 -432
-2 1042 1030
-3 1074-1091
-4  465 429
-5  609 -616
-6  501 -532
-7  542 532
-8 1186 1230
-9  194 -166
-10  0  4
-11  159 -144
-12  502 -471
-13  557 571
-14  283 277
-15  515 520
-16 1066 1068
-17  349 -335
-18  223 241
-19  322 -317
-20  510 542
-21  191 -186
-22  227 -241
-23  152 148
-24  312 328
-25  95 -107
-26  176 178
-27  84  -80

-28  0  15
-29  68  86
-30  99 -92
-31  199 188
-32  232 235
-33  0  -40
-34  117 102

H,K= 5, 1
 L FOBS FCAL
30  148 -169
29  97  95
28  121 119
27  0  30
26  319 326
25  0  -6
24  55  59
23  38  -54
22  413 -392
21  0  5
20  101  99

H,K= 9, 1
 L FOBS FCAL
19  63  71
18  0  -19
17  100 113
16  587 588
15  167 -160
14  321 -304
13  43  -35
12  199 210
11  0  17
10  804 799
9  215 -214
8  231 256
7  206 -208
6  965 -933
5  545 531
4  754 759
3  171 173
2  671 687
1  0  -21
0  730 746
-1  74  -77
-2  937 918
-3  91  -85
-4  500 508
-5  341 -350
-6  33  -49
-7  399 -412
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-9  432 -438
-10  593 -602
-11  656 667
-12  321 325
-13  400 414
-14  438 415
-15  71  81
-16  667 680
-17  30  -8
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-19  244 251
-20  73  -73
-21  34  -61
-22  34  -32
-23  136 -144
-24  270 272
-25  152 -163
-26  189 -180
-27  102 98
-28  0  -28
-29  0  -13
-30  180 190
-31  0  -18
-32  198 200
-33  0  -30

H,K=11, 1
 L FOBS FCAL
27  0  -18
26  44  -22
25  0  -29
24  119 -120
23  0  -15
22  0  -2
21  81  58
20  56  56
19  0  -18
18  0  15
17  9  69
16  253 254
15  86 -103
14  0  -21
13  75  80
12  602 605
11  126 -107
10  448 461
9  196 -214
8  141 -136
7  30  24
6  0  -30
5  275 256
4  865 851
3  76  62
2  183 193
1  415 426
0  157 163
-1  257 263
-2  453 -453
-3  97  104
-4  443 424
-5  366 -369
-6  40  -71
-7  111 -116
-8  64  -70
-9  175 -182
-10  411 -436
-11  73  -65

-12  727 738
-13  157 -158
-14  261 274
-15  186 198
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-17  133 127
-18  285 -292
-19  84  73
-20  339 341
-21  72  -93
-22  237 235
-23  0  -5
-24  66  -62
-25  0  -45
-26  0  -30
-27  40  -15
-28  380 381
-29  84  -76
-30  86  96
-31  0  5

H,K= 9, 1
 L FOBS FCAL
-4  72  87
-5  144 157
-6  236 228
-7  42  32
-8  59  81
-9  146 -125
-10  267 -268
-11  42  42
-12  93  93
-13  0  44
-14  105 104
-15  43  -27
-16  138 130
-17  132 -131

H,K= 0, 2
 L FOBS FCAL
0 1170 1153
-1  434 -418
-2  343 324
-3  546 -553
-4  434 -451
-5  589 573
-6 1272 1273
-7  220 251
-8  838 841
-9  238 218
-10  128 108
-11  601 584
-12 1030 1042
-13  522 -484
-14  290 -257
-15  822 841
-16  822 822
-17  430 -396
-18  348 -341
-19  270 -252
-20  257 -250
-21  80  -32
-22  139 -140
-23  360 379
-24  326 318
-25  115 -92
-26  53  -10
-27  66  -78
-28  39  47
-29  40  43
-30  109 104
-31  119 108
-32  183 186
-33  76  -85

H,K= 2, 2
 L FOBS FCAL
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31  43  13
30  84  -82
29  131 127
28  171 170
27  142 -153
26  159 152
25  0  -8
24  426 421
23  344 -353
22  413 -416
21  159 152
20  322 315
19  0  12
18  590 598
17  68  -66
16  243 258
15  29  -17
14  406 -384
13  415 417
12  418 426
11  186 -187
10  548 563
9  58  80
8  656 666
7  361 340
6 1093 1041
5  204 -179
4  111 103
3 1301 1308
2 1350 1339
1  171 165
0  317 277
-1 1210-1170
-2 2079-2246
-3  795 749
-4  324 -300
-5  256 -271
-6  856 -825
-7  248 218

-8  767 775
-9  796 -804
-10  138 -173
-11  806 804
-12 1079 1106
-13  124 102
-14  285 305
-15  110 -105
-16  413 463
-17  704 -711
-18  288 -277
-19  135 124
-20  32  53
-21  126 127
-22  255 272
-23  239 -258
-24  180 190
-25  149 -146
-26  83  81
-27  148 158
-28  103 104
-29  144 143
-30  164 167
-31  59  -66
-32  135 122
-33  158 -141

H,K= 4, 2
 L FOBS FCAL
30  44  58
29  61  84
28  256 268
27  82  -83
26  40  -13
25  39  50
24  67  51
23  38  -62
22  164 146
21  254 243
20  742 743
19  59 -136
18  94  110
17  156 -164
16  648 -647
15  338 336
14  90  -76
13  147 139
12  152 153
11  262 -258
10  297 -279
9  239 -239
8  58  -58
7  0  16
6  466 454
5  581 584
4 1731 1739
3  735 -735
2  219 194
1  82  -88
0  198 186
-1  368 -345
-2  974 -951
-3  50  629
-4  995 998
-5 1276-1293
-6  23  -37
-7  269 -252
-8  527 531
-9  186 166
-10  263 236
-11  589 600
-12 1042 1067
-13  315 -311
-14  533 543
-15  175 170
-16  310 -309
-17  543 548
-18  184 176
-19  64  62
-20  421 412
-21  337 -322
-22  182 177
-23  0  -5
-24  81  68
-25  111 110
-26  53  -70
-27  164 148
-28  194 214
-29  151 -152
-30  41  -46
-31  60  53
-32  43  -70
-33  0  34

H,K= 6, 2
 L FOBS FCAL
27  43  -49
26  135 -150
25  84  93
24  217 224
23  57  53
22  411 412
21  185 -188
20  75  90
19  165 -179
18  130 -145
17  154 191
16  278 279
15  76  78
14  223 236
13  173 -163
12  55  66
11  469 -479
10  562 -550
9  441 441

8  726 724
7  92  -86
6  790 798
5  135 -133
4  771 773
3  391 -390
2  655 -657
1 -2  61  -64
0  957 951
-1  0  -17
-2  601 588
-3  231 -231
-4  270 293
-5  0  14
-6  61  -45
-7  0  -10
-8  62  45
-9  201 -204
-10  251 -248
-11  203 202
-12  513 517
-13  53  -65
-14  195 202
-15  93  95
-16  77  100
-17  129 -143
-18  229 -223
-19  187 183
-20  180 178
-21  58  60
-22  59  57
-23  0  -19
-24  95  -88
-25  43  -50
-26  76  -71

H,K=12, 2
 L FOBS FCAL
20  149 154
19  174 -172
18  164 -165
17  484 484
16  185 179
15  309 303
14  292 286
13  473 -449
12  183 -143
11  239 241
10  123 124
9  498 464
8  649 647
7  0  5
6  498 459
5  175 -179
4  156 158
3  633 -593
2  326 -294
1  759 762
0  178 183
-1  492 468
-2  234 230
-3  0  -15
-4  913 920
-5 1545-1581
-6  818 -808
-7 1312 1314
-8  831 853
-9  587 -591
-10  297 405
-11  787 -773
-12  61  71
-13  288 -302
-14  168 163
-15  320 313
-16  546 540

H,K= 1, 3
 L FOBS FCAL
32  44  -40
31  106 98
30  85  70
29  72  68
28  163 151
27  264 -250
26  95  -79
25  228 223
24  181 167
23  51  48
22  259 265
21  34  20
20  342 320
19  550 -558
18  335 -347
17  189 196
16  0  15
15  390 -392
14  103 -99
13  234 251
12  607 610
11  292 -282
10  562 582
9  25  -24
8  939 969
7  175 152
6 1205 1218
5  198 200
4  550 568
3  696 661
2  37  -10
1  303 -259
0  880 -850
-1  540 541
-2  303 -265
-3 1184 1184
-4  857 877
-5  580 -596
-6  209 212
-7  172 203
-8  645 654
-9  249 -237
-10  303 314
-11  418 416

5  0  -5
4  163 166
3  0  34
2  477 476
1  164 -169
0  0  -12
-1  0  9
-2  61  -64
-3  260 270
-4  608 607
-5  71  -89
-6  269 276
-7  0  -10
-8  62  45
-9  201 -204
-10  251 -248
-11  203 202
-12  513 517
-13  53  -65
-14  195 202
-15  93  95
-16  77  100
-17  129 -143
-18  229 -223
-19  187 183
-20  180 178
-21  58  60
-22  59  57
-23  0  -19
-24  95  -88
-25  43  -50
-26  76  -71

H,K= 3, 3
 L FOBS FCAL
21  51  44
20  149 154
19  174 -172
18  164 -165
17  484 484
16  185 179
15  309 303
14  292 286
13  473 -449
12  183 -143
11  239 241
10  123 124
9  498 464
8  649 647
7  0  5
6  498 459
5  175 -179
4  156 158
3  633 -593
2  326 -294
1  759 762
0  178 183
-1  492 468
-2  234 230
-3  0  -15
-4  913 920
-5 1545-1581
-6  818 -808
-7 1312 1314
-8  831 853
-9  587 -591
-10  297 405
-11  787 -773
-12  61  71
-13  288 -302
-14  168 163
-15  320 313
-16  546 540

H,K= 5, 3
 L FOBS FCAL
28  44  47
27  106 120
26  153 158
25  59  -49
24  115 137
23  191 -208
22  0  -21
21  54  77
20  144 152
19  227 -212
18  60  -35
17  330 339
16  235 243
15  57  13
14  164 176
13  39  -50
12  86  76
11  244 -260
10  322 -320
9  474 474
8  64  45
7  193 189
6  279 266
5  250 -247
4  170 174
3  320 -298
2  60  -53

1  92  100
0  109  54
-1  69  94
-2  321 318
-3  424 -420
-4  124 113
-5  396 -393
-6  147 -140
-7  336 339
-8  431 328
-9  50  57
-10  371 383
-11  0  2
-12  322 311
-13  281 -293
-14  122 -133
-15  306 288
-16  113 115
-17  0  -34
-18  0  23
-19  117 114
-20  168 166
-21  279 -259
-22  41  -43
-23  72  89
-24  73  80
-25  121 124
-26  174 165
-27  44  -2

H,K=11, 3
 L FOBS FCAL
15  269 -274
12  60  -55
11  158 160
10  125 136
9  41  33
8  232 233
7  163 -161
6  57  68
5  0  24
4  0  24
3  112 121
2  88  86
1  135 136
0  210 220
-1  129 -143
-2  55  67
-3  39  -54
-4  39  42
-5  0  -46
0  19
-7  348 351
-8  382 381
-9  288 -289
-10  0  9
-11  68  61
-12  40  -4
-13  69  62
-14  57  -46
-15  264 257
-16  82  106
-17  59  -54
-18  42  25
-19  60  -81
-20  0  -32
-21  0  10
-22  44  23

H,K=13, 3
 L FOBS FCAL
4  76  84
3  0  20
2  0  35
1  97  123
0  87  95
-1  156 -154
-2  86  -89
-3  122 144
-4  48  66
-5  0  -5
-6  86  81
-7  61  -54
-8  97  85
-9  260 -259
-10  87  -90
-11  62  84
-12  0  29
-13  76  83

H,K= 0, 4
 L FOBS FCAL
0 1211 1207
-1 1170-1208
-2  596 589
-3  350 340
-4  178 201
-5  207 188
-6  0  -10
-7  210 228
-8  180 175
-9  130 -141
-10  117 119
-11  113 129
-12  0  -29
-13  59  -61
-14  0  -15
-15  658 662
-16  384 392
-17  0  -17
-18  315 310
-19  233 -232
-20  60  -53
-21  213 207
```

-22	51	-42
-23	286	270
-24	198	203
-25	309	-302
-26	164	163
-27	128	-121
-28	0	-12
-29	85	-79
-30	0	5
-31	193	184

H,K= 2, 4

L	FOBS	FCAL
30	44	24
29	87	91
28	60	82
27	0	21
26	0	-1
25	0	3
24	68	-49
23	226	-237
22	53	35
21	312	310
20	343	344
19	195	205
18	374	367
17	385	-384
16	236	233
15	383	-386
14	177	188
13	631	643
12	341	330
11	283	-277
10	0	-38
9	585	585
8	0	-29
7	360	-363
6	60	26
5	440	447
4	368	398
3	533	490
2	619	612
1	321	330
0	399	392
-1	948	-936
-2	171	-166
-3	831	864
-4	135	122
-5	559	545
-6	456	479
-7	298	-299
-8	227	217
-9	544	-537
-10	62	-58
-11	0	-47
-12	184	200
-13	0	34
-14	428	447
-15	279	-285
-16	71	93
-17	549	-561
-18	220	-222
-19	447	449
-20	120	114
-21	146	144
-22	346	345
-23	0	-5
-24	227	203
-25	346	-347
-26	40	17
-27	162	160
-28	124	115
-29	0	-8
-30	149	147
-31	44	-54

H,K= 4, 4

L	FOBS	FCAL
28	0	14
27	106	-108
26	0	-18
25	42	24
24	71	68
23	126	113
22	78	83
21	491	500
20	225	213
19	370	-361
18	157	168
17	132	-137
16	151	160
15	201	195
14	137	132
13	492	504
12	178	135
11	621	-630
10	0	25
9	0	10
8	137	119
7	51	48
6	294	291
5	372	357
4	400	382
3	823	-846
2	0	-3
1	807	-761
0	214	-205
-1	242	240
-2	153	175
-3	622	590
-4	465	452
-5	314	-298
-6	314	309
-7	233	-258
-8	341	334
-9	148	148
-10	599	603
-11	493	490
-12	575	568
-13	887	-889
-14	122	-123
-15	240	-234
-16	224	-234
-17	238	243
-18	113	118
-19	541	534
-20	256	247
-21	314	-299
-22	0	-2
-23	192	178
-24	94	57
-25	88	88
-26	150	145
-27	153	180
-28	125	120
-29	154	-165
-30	43	-49
-31	108	-105

H,K= 6, 4

L	FOBS	FCAL
25	240	244
24	43	33
23	0	-2
22	59	74
21	158	-151
20	69	78
19	341	-323
18	0	-17
17	360	375
16	37	42
15	0	-8
14	161	144
13	253	-268
12	184	181
11	291	-301
10	200	189
9	581	570
8	373	394
7	282	283
6	429	434
5	658	-656
4	89	93
3	513	-503
2	111	-100
1	724	727
0	159	170
-1	0	-0
-2	86	95
-3	175	-163
-4	0	17
-5	0	41
-6	247	244
-7	881	879
-8	496	507
-9	138	136
-10	204	198
-11	0	-11
-12	46	-40
-13	618	-616
-14	75	-78
-15	514	511
-16	159	182
-17	35	-41
-18	72	95
-19	258	-266
-20	0	22
-21	131	-144
-22	77	94
-23	263	261
-24	169	172
-25	41	-7
-26	41	27
-27	84	-83
-28	0	-11
-29	116	-118

H,K= 8, 4

L	FOBS	FCAL
21	0	16
20	61	-30
19	268	274
18	59	56
17	0	-6
16	114	112
15	311	-314
14	56	58
13	164	158
12	93	98
11	299	301
10	193	191
9	322	317
8	277	263
7	281	-296
6	101	103
5	61	-38
4	0	37
3	374	357
2	77	96
1	178	174
0	137	118
-1	914	-914
-2	48	-28
-3	201	205
-4	167	182
-5	108	119
-6	149	162
-7	154	147
-8	60	64
-9	357	-369
-10	35	14
-11	61	67
-12	156	161
-13	81	77
-14	146	149
-15	133	135
-16	167	162
-17	403	-407
-18	167	155
-19	135	-149
-20	177	166
-21	113	116
-22	71	68
-23	72	70
-24	0	7
-25	121	-126
-26	43	5
-27	0	27

H,K=10, 4

L	FOBS	FCAL
16	0	-1
15	0	13
14	0	-15
13	175	203
12	94	89
11	223	-223
10	41	58
9	0	-29
8	57	53
7	98	-100
6	0	14
5	366	366
4	160	139
3	55	-67
2	196	187
1	245	-239
0	209	221
-1	312	-313
-2	114	120
-3	284	282
-4	76	91
-5	194	-193
-6	54	51
-7	148	-149
-8	66	72
-9	0	24
-10	39	20
-11	344	349
-12	68	44
-13	153	139
-14	120	131
-15	90	-92
-16	168	158
-17	82	-98
-18	59	51
-19	173	184
-20	0	-9
-21	43	-11
-22	0	22
-23	0	-60

H,K=12, 4

L	FOBS	FCAL
8	44	-18
7	139	124
6	0	59
5	179	191
4	161	170
3	96	-105
2	128	131
1	60	75
0	42	52
-1	127	124
-2	60	47
-3	42	38
-4	111	94
-5	206	-227
-6	42	34
-7	60	-27
-8	85	-68
-9	175	174
-10	0	12
-11	121	130
-12	167	158
-13	216	-201
-14	62	80
-15	0	14
-16	44	-28

H,K= 1, 5

L	FOBS	FCAL
29	0	49
28	75	-61
27	316	-318
26	42	1
25	130	134
24	120	122
23	289	293
22	149	144
21	278	-275
20	52	62
19	367	-378
18	138	137
17	0	27
16	249	253
15	342	345
14	195	192
13	32	32
12	0	-23
11	639	-637
10	219	211
9	537	553
8	94	108
7	102	102
6	104	102
5	322	315
4	113	-114
3	1287	-1309
2	375	403
1	618	618
0	287	298
-1	505	498
-2	499	493
-3	702	732
-4	460	464
-5	766	-767
-6	468	475
-7	283	292
-8	29	-29
-9	875	868
-10	187	-188
-11	351	-369
-12	0	38
-13	362	-368
-14	33	27
-15	47	40
-16	0	7
-17	277	278
-18	255	275
-19	172	168
-20	323	328
-21	522	-523
-22	215	195
-23	87	-73
-24	40	21
-25	99	101
-26	82	75
-27	133	134
-28	74	41
-29	368	-371

H,K= 3, 5

L	FOBS	FCAL
27	98	103
26	105	101
25	158	173
24	0	-13
23	129	-124
22	0	-19
21	175	-177
20	38	60
19	0	5
18	212	214
17	506	511
16	123	131
15	244	-251
14	327	340
13	34	-13
12	408	414
11	33	53
10	375	375
9	1087	1091
8	132	-160
7	781	-799
6	0	-29
5	30	-14
4	202	-207
3	42	34
2	88	-93
1	248	236
0	307	309
-1	0	-16
-2	593	608
-3	783	-800
-4	546	554
-5	0	-10
-6	351	353
-7	543	542
-8	177	183
-9	370	-371
-10	70	79
-11	666	-676
-12	111	-120
-13	149	151
-14	0	-5
-15	554	558
-16	249	244
-17	394	-394
-18	312	315
-19	0	19
-20	0	5
-21	281	-281
-22	127	128
-23	442	444
-24	80	79
-25	152	-141
-26	41	37
-27	152	-144
-28	0	-23
-29	0	8

H,K= 5, 5

L	FOBS	FCAL
25	62	-59
24	61	14
23	154	-164
22	42	31
21	267	262
20	114	-107
19	105	-99
18	55	40
17	207	190
16	146	124
15	596	-605
14	361	365
13	157	168
12	283	277
11	254	260
10	209	204
9	225	-234
8	111	99
7	467	-465
6	33	-10
5	399	403
4	128	-137
3	247	239
2	84	102
1	438	-470
0	233	253
-1	169	-160
-2	163	176
-3	0	-11
-4	307	310
-5	241	221
-6	365	369
-7	189	190
-8	0	-2
-9	684	-675
-10	123	75
-11	649	667
-12	126	126
-13	118	110
-14	261	264
-15	222	169
-16	36	3
-17	407	-419
-18	52	45
-19	345	324
-20	54	53
-21	145	134
-22	68	80
-23	40	19
-24	115	-65
-25	212	-214
-26	84	50
-27	0	18
-28	124	142

H,K= 7, 5

L	FOBS	FCAL
22	0	-34
21	185	198
20	43	-39
19	190	-196
18	72	70
17	41	-55
16	0	20
15	120	-128
14	142	131
13	190	190
12	179	191
11	0	-8
10	144	166
9	340	-339
8	179	178
7	355	364
6	179	177
5	448	439
4	122	125
3	178	-185
2	104	102
1	0	-25
0	0	5
-1	34	-39
-2	146	154
-3	527	512
-4	0	3
-5	366	-387
-6	0	13
-7	130	146
-8	93	76
-9	176	-166
-10	375	374
-11	379	398
-12	125	127
-13	361	-366
-14	104	105
-15	205	-205
-16	125	125
-17	38	-51
-18	160	146
-19	163	155
-20	0	-23
-21	0	-4
-22	0	-18
-23	201	-189
-24	112	110
-25	75	61
-26	124	121

H,K= 9, 5

L	FOBS	FCAL
17	89	98
16	0	-3
15	156	158
14	0	24
13	73	-97
12	0	14
11	206	-205
10	122	111
9	156	152
8	187	182
7	131	128
6	180	191
5	95	84
4	102	81
3	515	-504
2	199	186
1	194	198
0	0	25
-1	54	-53
-2	0	-15
-3	100	106
-4	53	-52
-5	456	-447
-6	221	220
-7	232	243
-8	133	147
-9	149	133
-10	67	78
-11	110	-159
-12	111	94
-13	189	-190
-14	164	158
-15	57	-52
-16	41	43
-17	159	169
-18	0	-38
-19	0	28
-20	43	55
-21	114	-114
-22	115	133
-23	146	128

H,K=11, 5

L	FOBS	FCAL
9	257	267
8	44	48
7	281	-285
6	143	156
5	0	-23
4	85	103
3	104	-110
2	60	77
1	279	278
0	0	-31
-1	72	-77
-2	93	85
-3	204	-198
-4	132	128
-5	172	158
-6	42	57
-7	310	298
-8	42	19
-9	59	-27
-10	84	95
-11	170	-182
-12	60	46
-13	96	98
-14	61	-71
-15	163	160
-16	44	-16
-17	117	-111

H,K= 0, 6

L	FOBS	FCAL
0	372	-353
-1	894	-886
-2	514	508
-3	224	-211
-4	420	442
-5	515	539
-6	105	-106
-7	449	457
-8	368	-380
-9	212	-242
-10	188	177
-11	58	-33
-12	346	336
-13	186	186
-14	375	378
-15	419	422
-16	73	-73
-17	369	-375
-18	164	163
-19	288	-301
-20	151	158
-21	119	125
-22	81	3
-23	281	269
-24	151	-133
-25	185	-200
-26	106	132
-27	0	-1

H,K= 2, 6

L	FOBS	FCAL
26	0	9
25	137	-138
24	60	-64
23	272	-278
22	189	184
21	286	281
20	56	-47
19	203	199
18	77	-86
17	387	-379
16	278	275
15	151	-163
14	473	470
13	610	614
12	167	-168
11	0	-34
10	0	11
9	67	-73
8	119	134
7	167	-157
6	391	408
5	628	625
4	0	9
3	231	230
2	109	112
1	361	-380
0	357	380
-1	593	-594
-2	609	633
-3	661	684
-4	283	-284
-5	106	102
-6	150	-148
-7	341	-347
-8	219	235
-9	136	-127
-10	367	373
-11	486	491
-12	34	38
-13	0	22
-14	202	209
-15	250	-266
-16	189	174
-17	433	-419
-18	293	286
-19	241	250
-20	55	-52
-21	56	-61
-22	0	21
-23	108	-106
-24	42	41
-25	175	-176
-26	136	138
-27	158	159

H,K= 4, 6

L	FOBS	FCAL
24	63	72
23	130	129
22	60	72
21	188	185
20	41	-47
19	307	-320
18	233	230
17	56	-49
16	155	160
15	267	269
14	0	-18
13	153	168
12	0	-26
11	461	-468
10	409	421
9	231	228
8	70	67
7	236	250
6	34	56
5	148	140
4	106	95
3	532	-545
2	408	415
1	128	-113
0	93	96
-1	104	96
-2	47	39
-3	0	-9
-4	47	54
-5	491	-496
-6	349	355
-7	0	-24
-8	76	71
-9	76	92
-10	134	129
-11	342	333
-12	61	-71
-13	335	-338
-14	173	174
-15	52	71
-16	74	63
-17	242	242
-18	77	75
-19	233	223
-20	39	-21
-21	238	-243
-22	141	155
-23	0	-31
-24	60	78
-25	0	18
-26	62	80
-27	77	83

H,K= 6, 6

L	FOBS	FCAL
21	117	-106
20	0	43
19	149	-154
18	120	58
17	204	200
16	71	-76
15	122	-131
14	120	130
13	142	-139
12	78	81
11	176	-180
10	147	173
9	238	252
8	53	70
7	0	43
6	172	141
5	166	-187
4	0	7
3	95	-95
2	87	91
1	507	507
0	71	-58
-1	0	13
-2	271	267
-3	0	-11
-4	162	170
-5	133	-121
-6	262	247
-7	160	168
-8	88	103
-9	89	-74
-10	73	85
-11	37	-24
-12	149	-129
-13	271	-258
-14	157	165
-15	378	374
-16	0	15
-17	197	191
-18	105	57
-19	114	-125
-20	164	147
-21	138	-133
-22	227	217
-23	86	74
-24	0	16
-25	62	-63

H,K= 8, 6

L	FOBS	FCAL
17	77	77
16	0	1
15	106	-137
14	96	104
13	60	50
12	94	93
11	0	26
10	278	278
9	141	154
8	40	25
7	211	-207
6	0	-15
5	130	-145
4	68	60
3	236	235
2	122	106
1	374	365
0	86	-89
-1	294	-292
-2	245	261
-3	54	75
-4	223	217
-5	38	41
-6	243	237
-7	0	23
-8	0	0
-9	365	-356
-10	39	49
-11	209	-214
-12	56	55
-13	57	48
-14	99	98
-15	191	204
-16	41	-50
-17	172	-170
-18	179	173
-19	43	-38
-20	129	131
-21	131	123
-22	44	22

H,K=10, 6

L	FOBS	FCAL
9	146	-149
8	0	-15
7	267	-269
6	178	178
5	148	158
4	43	5
3	42	59
2	94	-77
1	178	-169
0	0	41
-1	162	-163
-2	283	276
-3	364	354
-4	72	5
-5	59	65
-6	0	13
-7	162	-168
-8	59	46
-9	119	-123
-10	112	117
-11	225	209
-12	0	-26
-13	0	38
-14	0	30
-15	131	-125
-16	76	69

H,K= 1, 7

L	FOBS	FCAL
24	63	82
23	75	86
22	0	-1
21	42	59
20	200	-204
19	340	-333
18	274	282
17	69	69
16	78	-71
15	102	118
14	38	-55
13	100	108
12	118	-124
11	303	-370
10	548	553
9	36	-39
8	433	431
7	326	325
6	86	-113
5	35	-34
4	0	-34
3	201	-200
2	215	227
1	59	68
0	168	179
-1	414	425
-2	235	-244
-3	119	112
-4	278	-286
-5	429	-435
-6	669	674
-7	211	209
-8	215	221
-9	147	136
-10	63	74
-11	0	15
-12	117	-118
-13	314	-297
-14	522	536
-15	230	246
-16	55	12
-17	39	-36
-18	113	124
-19	0	20
-20	116	-130
-21	177	-198
-22	159	170
-23	0	-43
-24	170	164

H,K= 3, 7

L	FOBS	FCAL
22	125	133
21	144	-151
20	74	79
19	0	18
18	72	91
17	338	347
16	210	-200
15	80	54
14	68	-54
13	295	-302
12	435	431
11	126	123
10	209	203
9	257	260
8	127	-128
7	203	-197
6	284	292
5	160	-164
4	333	335
3	100	106
2	247	249
1	384	369
0	136	-137
-1	86	-96
-2	244	258
-3	122	-124
-4	35	48
-5	375	-383
-6	458	477
-7	329	321
-8	486	-505
-9	277	-273
-10	137	145
-11	105	-97
-12	257	275
-13	53	64
-14	236	225
-15	145	155
-16	0	-5
-17	40	-35
-18	107	119
-19	116	-120
-20	117	125
-21	73	-88
-22	74	73
-23	61	59
-24	108	-92

H,K= 5, 7

L	FOBS	FCAL
19	181	177
18	43	38
17	0	3
16	0	11
15	182	-183
14	170	170
13	41	43
12	98	102
11	164	175
10	118	-137
9	183	-182
8	116	-106
7	450	-457
6	451	456
5	309	297
4	155	-167
3	37	48
2	306	317
1	148	155
0	83	82
-1	276	-273
-2	383	379
-3	0	10
-4	0	-4
-5	64	58
-6	0	-47
-7	65	88
-8	258	-256
-9	204	-208
-10	153	168
-11	54	60
-12	123	137
-13	337	330
-14	40	-37
-15	89	71
-16	151	148
-17	153	-143
-18	203	206
-19	119	-93
-20	95	81
-21	61	65
-22	0	-4
-23	63	60

H,K= 7, 7

L	FOBS	FCAL
15	0	-0
14	222	231
13	240	234
12	171	-160
11	164	-160
10	42	-14
9	124	-132
8	41	-29
7	82	-8
6	243	226
5	362	367
4	170	-158
3	98	-99
2	235	242
1	125	-111
0	219	220
-1	39	48
-2	239	232
-3	219	226
-4	39	20
-5	0	-8
-6	56	-59
-7	305	-300
-8	178	168
-9	0	12
-10	121	136
-11	226	226
-12	41	-28
-13	41	-23
-14	59	81
-15	178	-186
-16	104	108
-17	113	-102
-18	188	190
-19	223	231
-20	132	-131

H,K= 9, 7

L	FOBS	FCAL
9	99	120
8	88	72
7	98	119
6	0	-40
5	106	-102
4	0	-44
3	227	-218
2	165	173
1	0	25
0	180	187
-1	243	252
-2	85	-72
-3	104	-101
-4	0	-5
-5	296	-274
-6	275	264
-7	120	114
-8	85	90
-9	128	114
-10	0	23
-11	75	-87
-12	61	-74
-13	255	-265
-14	197	195
-15	172	174

H,K= 0, 8

L	FOBS	FCAL
0	328	-321
-1	254	-216
-2	150	153
-3	234	-226
-4	296	287
-5	113	86
-6	0	11
-7	85	53
-8	102	-109
-9	129	-122
-10	260	253
-11	112	88
-12	40	37
-13	114	108
-14	318	330
-15	143	143
-16	270	-270
-17	146	-150
-18	121	93
-19	61	-29
-20	152	147
-21	44	57

H,K= 2, 8

L	FOBS	FCAL
19	98	112
18	97	-95
17	96	-97
16	0	17
15	162	-175
14	293	285
13	92	93
12	146	-143
11	40	26
10	0	-29
9	118	-136
8	55	70
7	0	-34
6	306	306
5	192	202
4	331	322
3	255	250
2	66	-78
1	65	-63
0	93	-92
-1	151	-140
-2	480	487
-3	178	163
-4	165	-170
-5	0	-28
-6	0	31
-7	38	-66
-8	0	0
-9	129	-126
-10	544	546
-11	97	89
-12	89	74
-13	40	-56
-14	41	54
-15	92	-98
-16	59	-62
-17	73	-75
-18	196	199
-19	0	27
-20	0	-14
-21	77	67

H,K= 4, 8

L	FOBS	FCAL
17	0	-46
16	287	278
15	189	194
14	43	-46
13	42	51
12	237	-221
11	161	-161
10	136	136
9	82	-85
8	295	292
7	90	92
6	271	274
5	79	56
4	177	-177
3	222	-213
2	271	264
1	55	-44
0	135	133
-1	39	38
-2	110	172
-3	170	169
-4	434	-435
-5	78	-66
-6	167	167
-7	39	-37
-8	254	235
-9	0	6
-10	251	246
-11	81	80
-12	168	-167
-13	71	-77
-14	42	45
-15	94	-160
-16	220	229
-17	43	51
-18	43	-32
-19	98	102

H,K= 6, 8

L	FOBS	FCAL
13	44	-65
12	0	-21
11	0	-50
10	353	344
9	142	126
8	95	-81
7	42	-28
6	73	-67
5	156	-153
4	41	23
3	189	-180
2	504	513
1	193	180
0	209	-204
-1	91	100
-2	142	-120
-3	0	-22
-4	82	82
-5	41	-32
-6	263	266
-7	92	93
-8	83	72
-9	177	164
-10	103	-124
-11	94	-82
-12	42	40
-13	165	-160
-14	317	328
-15	75	79
-16	0	-7
-17	77	84

H,K= 8, 8

L	FOBS	FCAL
5	88	-78
4	275	279
3	124	130
2	0	-9
1	75	79
0	168	-168
-1	168	-163
-2	274	293
-3	123	-107
-4	264	252
-5	106	112
-6	61	-61
-7	44	32
-8	124	-117
-9	158	-157
-10	132	129
-11	44	-37

H,K= 1, 9

L	FOBS	FCAL
15	77	77
14	0	-29
13	0	-8
12	183	-180
11	74	-76
10	240	240
9	0	23
8	0	45
7	110	117
6	101	100
5	92	-88
4	213	-220
3	142	-141
2	227	232
1	41	48
0	71	89
-1	195	207
-2	153	157
-3	0	-0
-4	169	-180
-5	92	-91
-6	350	351
-7	41	19
-8	246	253
-9	73	57
-10	60	-68
-11	74	-81
-12	121	-110
-13	106	-101
-14	75	87
-15	0	29

H,K= 3, 9

L	FOBS	FCAL
12	153	142
11	98	98
10	363	369
9	74	30
8	234	-234
7	85	-89
6	42	30
5	73	-92
4	42	52
3	72	102
2	256	257
1	72	82
0	0	-5
-1	41	-43
-2	138	-133
-3	72	-48
-4	239	221
-5	42	41
-6	490	488
-7	0	-1
-8	119	-116
-9	73	-83
-10	135	-143
-11	61	-70
-12	184	186
-13	0	25
-14	152	163
-15	44	40

H,K= 5, 9

L	FOBS	FCAL
8	166	-152
7	44	-5
6	347	354
5	43	31
4	115	106
3	0	13
2	178	-167
1	43	-40
0	142	-133
-1	0	-25
-2	219	201
-3	43	18
-4	227	218
-5	0	17
-6	86	-96
-7	0	-1
-8	242	-237
-9	44	34
-10	409	410
-11	0	18

H,K= 0,10

L	FOBS	FCAL
0	334	-331
-1	76	66
-2	271	268
-3	76	-81
-4	159	154
-5	125	66

H,K= 2,10

L	FOBS	FCAL
2	44	-46
1	147	-141
0	44	-10
-1	63	28
-2	388	408
-3	0	-14

Table 2. Atomic coordinates in $MgSO_4.6H_2O$.

	Atom	x	y	z
	Mg(1)	0	0	0
	Mg(2)	0	0.9425	$\frac{1}{4}$
	S	0.8659	0.4490	0.1241
Sulfate oxygens	O(1)	0.7747	0.5986	0.1361
	O(2)	0.9834	0.4442	0.1665
	O(3)	0.9069	0.4854	0.0692
	O(4)	0.7961	0.2688	0.1211
Water about Mg(1)	O(5)	0.5852	0.7125	0.0483
	O(6)	0.5393	0.3162	0.0640
	O(7)	0.3126	0.5464	0.0231
Water about Mg(2)	O(8)	0.8887	0.1486	0.2820
	O(9)	0.8884	0.7405	0.2811
	O(10)	0.8598	0.9435	0.1799
Water (5)	H(1)	0.643	0.698	0.076
	H(2)	0.539	0.806	0.045
Water (6)	H(3)	0.495	0.232	0.060
	H(4)	0.614	0.340	0.093
Water (7)	H(5)	0.304	0.650	0.055
	H(6)	0.271	0.544	0.014
Water (8)	H(7)	0.840	0.092	0.312
	H(8)	0.937	0.235	0.296
Water (9)	H(9)	0.940	0.651	0.291
	H(10)	0.820	0.733	0.275
Water (10)	H(11)	0.849	0.831	0.164
	H(12)	0.847	0.033	0.164

Estimated standard deviations are: for Mg(2), $\sigma(y) = 0.0002$; for S, $\sigma(x) = 0.00006$, $\sigma(y) = 0.00008$, $\sigma(z) = 0.00002$; for oxygen, $\sigma(x) = 0.0002$, $\sigma(y) = 0.0003$, $\sigma(z) = 0.0001$.

Table 3. Anisotropic thermal parameters (each multiplied by 10^4) and root mean square amplitudes of vibration in $MgSO_4.6H_2O$.

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	u, Å
Mg(1)	45	86	8.7	2	-1	-3	0.16
Mg(2)	46	72	7.8	(0)[a]	2	(0)[a]	0.15
S	46	72	9.8	0	-1	-1	0.16
O(1)	64	103	12.4	23	4	-1	0.18
O(2)	79	107	17.6	10	-17	-5	0.21
O(3)	81	120	13.2	0	10	-1	0.19
O(4)	68	85	15.4	-19	-4	6	0.19
O(5)	67	129	13.6	17	-5	-12	0.19
O(6)	87	175	19.0	-51	-15	26	0.23
O(7)	54	216	16.7	7	3	-21	0.21
O(8)	67	94	12.6	-2	6	-7	0.18
O(9)	61	113	16.0	-5	5	12	0.19
O(10)	103	103	10.7	-8	-8	2	0.20

[a]Zero because of 2-fold axis.

Table 4. Isotropic thermal parameters for H in $MgSO_4.6H_2O$.

Atom	B, $Å^2$	Atom	B, $Å^2$	Atom	B, $Å^2$
H(1)	1.9	H(5)	5.6	H(9)	5.9
H(2)	5.2	H(6)	1.9	H(10)	3.1
H(3)	1.9	H(7)	4.3	H(11)	2.6
H(4)	5.7	H(8)	1.3	H(12)	2.0

Table 5. Interatomic distances and standard deviations in $MgSO_4 \cdot 6H_2O$.

Atoms		Distance	σ
	Water octahedron about Mg(1)		
Mg(1)	- 2 O(5)	2.046 Å	0.002 Å
	- 2 O(6)	2.044	0.003
	- 2 O(7)	2.080	0.002
O(5)	- O(6)	2.930	0.004
	- O(6)	2.854	0.004
	- O(7)	2.986	0.003
	- O(7)	2.847	0.003
O(6)	- O(7)	2.889	0.004
	- O(7)	2.943	0.003
	Water octahedron about Mg(2)		
Mg(2)	- 2 O(8)	2.083	0.002
	- 2 O(9)	2.054	0.002
	- 2 O(10)	2.059	0.003
O(8)	- O(8)	2.917	0.004
	- O(9)	2.943	0.003
	- O(10)	2.876	0.003
	- O(10)	2.973	0.003
O(9)	- O(9)	2.896	0.003
	- O(10)	2.850	0.003
	- O(10)	2.972	0.003

Table 5 (cont.)

Sulfate ion

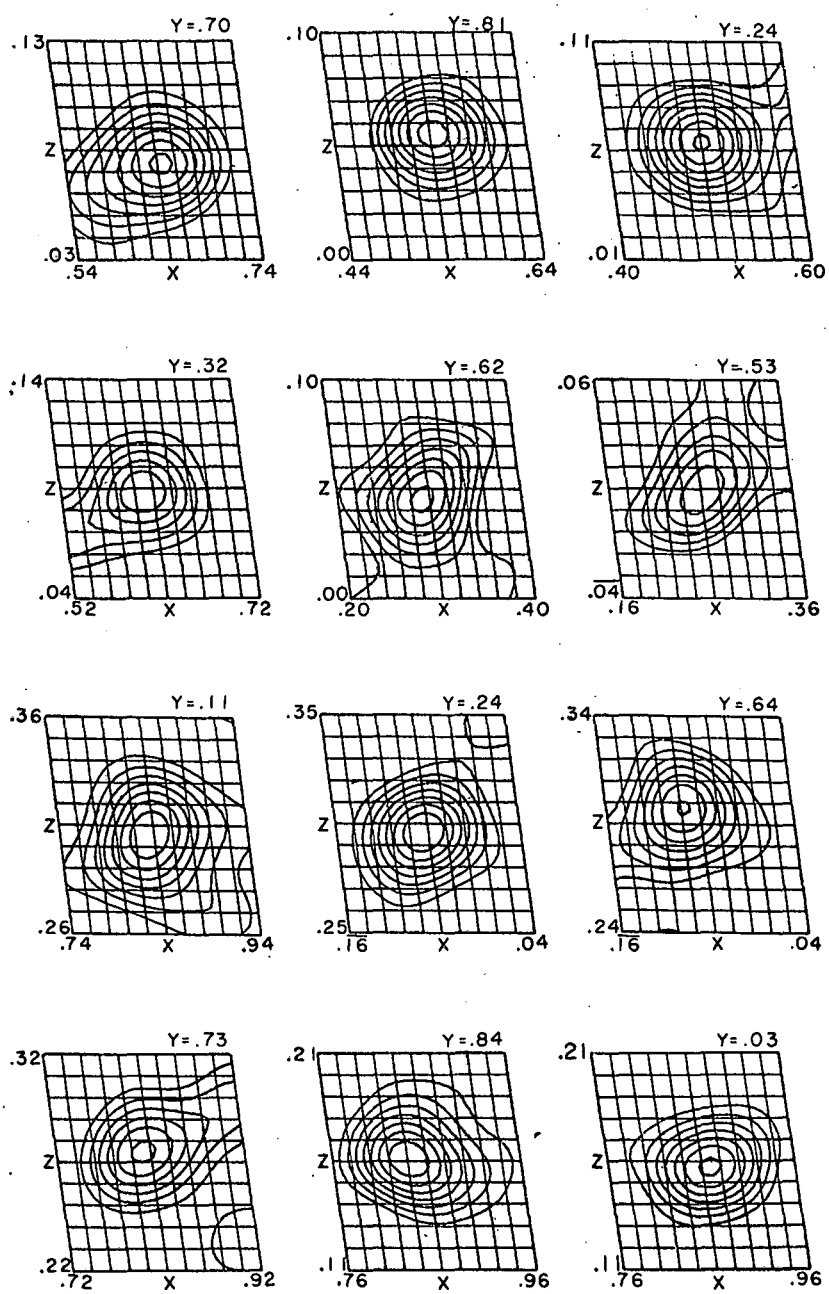
S	- O(1)	1.476	0.002
	- O(2)	1.460	0.003
	- O(3)	1.482	0.002
	- O(4)	1.475	0.002

Hydrogen bonds

O(5) - H(1) -- O(1)	2.785	0.003
O(5) - H(2) -- O(3)	2.766	0.003
O(6) - H(3) -- O(3)	2.747	0.003
O(6) - H(4) -- O(4)	2.785	0.004
O(7) - H(5) -- O(4)	2.906	0.003
O(7) - H(6) -- O(3)	2.934	0.004
O(8) - H(7) -- O(1)	2.796	0.003
O(8) - H(8) -- O(2)	2.707	0.003
O(9) - H(9) -- O(2)	2.721	0.003
O(9) - H(10) -- O(8)	3.068	0.003
O(10) - H(11) -- O(1)	2.794	0.003
O(10) - H(12) -- O(4)	2.777	0.003

(Figure caption)

Fig. 1. Electron density sections through hydrogen atoms, with other atoms subtracted out. Contour interval approx. 0.1 e/Å^3; zero and negative contours omitted. Grid lines and contours were reproduced photographically from cathode ray tube of computer.



Hydrogen in $MgSO_4 \cdot 6H_2O$

MUB-1485

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