

On the Crystal Chemistry of Salt Hydrates. IV. The Refinement of the Crystal Structure of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (Epsomite)*

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The structure of orthorhombic $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ has been refined, using three-dimensional photographic X-ray data, to a final $R = 5.7\%$ for 1578 non-zero F_{hkl} . The results of Beevers & Schwartz for the isostructural compound $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ are confirmed by this refinement. The hydrogen atoms have been located and their positions refined. The mean values (and the estimated standard deviations of this mean) for the seven crystallographically different water molecules are: $102^\circ(5^\circ)$ for the angle H-O(w)-H, $0.99(4)$ Å for the distance O-H and $1.54(7)$ Å for the distance H-H. Two of the water molecules, which are coordinated to Mg^{2+} , act as acceptor atoms for hydrogen bonds. Their mean distance to Mg^{2+} is 2.09_6 Å and thus significantly longer than the mean distances Mg-O(w) of 2.05_0 Å of the other four water molecules in the coordination octahedron around Mg^{2+} .

Introduction

In connection with the crystal structure determination of monoclinic $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (III=Baur, 1964*b*) it seemed interesting to know in detail the structure of one of the corresponding orthorhombic heptahydrates. The structure of orthorhombic $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ has been reported by Beevers & Schwartz (1935) and is one of the classic hydrate structures which have been determined by the Manchester school. For the refinement the isostructural $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ has been chosen since this compound offers the best chance for finding the hydrogen atoms by X-ray diffraction. Furthermore, since the Mg^{2+} ion is spherical (contrary to some of the transition element ions which form the isostructural sulfate hydrates) it was hoped that any variations in bond length in the octahedral $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ configuration could be ascribed unequivocally to changes in the sum of electrostatic bonds received by the water oxygen atoms. Such variations can be expected from Pauling's electrostatic valence rule, as has been discussed previously in part I of this series (Baur, 1962).

Orthorhombic $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ is the stable phase in saturated aqueous solutions of MgSO_4 between 1.8 and 49.5 °C (*Gmelins Handbuch der anorganischen Chemie*, 1939). The corresponding mineral is called epsomite.

Experimental

Crystals of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ were grown at 40 °C from an aqueous solution. Large, well developed specimens were cut and ground to plates of approximate dimensions $0.2 \times 2.0 \times 2.0$ mm³ perpendicular to the crystal directions [100], [010], [001] and [110]. Using Zr-

filtered Mo $K\alpha$ radiation, 20 layers were recorded by the multiple-exposure technique on a precession camera: the zero through third layer perpendicular to [100], the zero through fifth layer perpendicular to [010], the zero layer perpendicular to [001] and the zero through eighth layer perpendicular to [110]. Thus the three-dimensional data are fairly complete within a sphere of the radius $\sin \theta/\lambda = 0.7$ Å⁻¹. Owing to the peculiarities of the geometry of the precession apparatus several hundred reflections lying outside this range could also be observed. Roughly 2700 intensities were estimated visually by comparison with a calibrated strip. The intensities were reduced to F_o with a Lorentz-polarization factor program written by the author in FORTRAN II. With this program the correction can be computed for crystals which have any symmetry and any orientation with respect to the camera. The formulas used are those of Waser (1951) and Burbank (1952). Especially for the low orders many intensities were observed up to four times on different films; the scaling of the data to one base was greatly facilitated. After averaging the structure factors, which were observed several times, 1595 independent reflections were obtained and used in the refinement. An additional 263 intensities were too weak to be observed. The cell constants were derived from the precession photographs taking Mo $K\alpha$ (mean) = 0.7107 Å.

The structure was refined by the method of least-squares on the IBM 7094 computer of the Brookhaven National Laboratory, using the local modification of the FORTRAN crystallographic least-squares program ORFLS (Busing, Martin & Levy, 1962*a*). Throughout the refinement the weighting scheme of Hughes (1941) was adopted. Also employed were the local modifications of the function and error program ORFFE (Busing, Martin & Levy, 1962*b*) and the Fourier synthesis program FORDAPER by Allan Zalkin.

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Crystal data

MgSO₄·7H₂O is orthorhombic, with $a=11.868(10)^*$, $b=11.996(10)$, $c=6.857(7)$ Å; $V=976(2)$ Å³, $Z=4$, $D_x=1.677(4)$ and $D_m=1.676$ g.cm⁻³ (Viola, 1923). The cell constants agree with those of Westenbrink (1926) who found $a=11.90$, $b=12.02$ and $c=6.87$ Å. The axial ratios $a:b:c$ calculated from the cell constants are 0.9894:1:0.5717 in accord with the values of 0.9892:1:0.5711 quoted by Groth (1908). For $h00$, $0k0$ and $00l$, h , k and l are found to be present only when even, thus confirming Westenbrink's choice of space group $P2_12_12_1$. All atoms lie in the fourfold general position: x, y, z ; $\frac{1}{2}-x, \bar{y}, \frac{1}{2}+z$; $\frac{1}{2}+x, \frac{1}{2}-y, \bar{z}$; $\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z$.

Refinement of structure

The parameters of Beevers & Schwartz (1935) yielded for 1000 observed structure factors with $\sin \theta/\lambda < 0.6$ Å⁻¹ an R value ($R = \Sigma |F_o| - |F_c| / \Sigma |F_o|$) of 0.26. After three cycles of least-squares refinement R dropped to 0.09. In one more cycle using all the observed 1595 F_o , R was lowered from 0.113 to 0.101. At this stage the data were rescaled using all the 2700 estimated reflections: in one cycle the 20 scale factors and 13 temperature factors were varied and R fell from 0.110 to 0.098. The data were averaged again employing the new scale factors. The 17 strongest reflections, which seemingly are affected by extinction, were left out of all the subsequent refinements (and R values) and the remaining 1578 F_o were refined in two cycles using anisotropic thermal parameters for all the atoms from an R of 0.088 to 0.062. In these anisotropic cycles 118 parameters were varied: 1 scale factor, 39 positional parameters and 78 thermal parameters.

The positions of the hydrogen atoms were arrived at in two ways. On one hand they were calculated assuming the known geometry of the water molecule

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

and assuming them to lie in the same plane with the water oxygen atoms and the oxygen atoms to which these water oxygen atoms are hydrogen bonded (as described in more detail in III). On inclusion of these positions in the structure factor calculation R fell from 0.062 to 0.057 (for all observed F_o). The difference in R is more striking when the corresponding R values for the 230 F_{hkl} (including non-observed F_o) with $\sin \theta/\lambda < 0.36$ Å⁻¹ are compared: they are 0.077 and 0.055. The 230 low order reflections were refined in two cycles, varying only the 42 positional parameters of the hydrogen atoms. The B of the isotropic temperature factor for the hydrogen atoms was chosen uniformly 1.3 Å² higher than the B of the corresponding water oxygen atoms and was not varied. The R value dropped insignificantly to 0.054. In-

Table 1. MgSO₄·7H₂O, *positional parameters and their standard deviations*

| Atom | x | y | z |
|-------|-----------|-----------|-----------|
| Mg | 0.4229(1) | 0.1063(1) | 0.0340(2) |
| S | 0.7266(1) | 0.1839(1) | 0.4905(1) |
| O(1) | 0.6853(4) | 0.0750(4) | 0.4279(7) |
| O(2) | 0.8506(3) | 0.1868(4) | 0.4821(6) |
| O(3) | 0.6884(3) | 0.2063(4) | 0.6904(6) |
| O(4) | 0.6808(3) | 0.2716(4) | 0.3605(6) |
| O(w1) | 0.2655(3) | 0.1746(4) | 0.0038(6) |
| O(w2) | 0.4716(3) | 0.2478(3) | 0.1992(6) |
| O(w3) | 0.4691(3) | 0.1758(4) | 0.7796(6) |
| O(w4) | 0.5828(3) | 0.0463(4) | 0.0773(6) |
| O(w5) | 0.3761(3) | 0.9620(3) | 0.8889(6) |
| O(w6) | 0.3622(3) | 0.0342(4) | 0.2907(6) |
| O(w7) | 0.4916(4) | 0.4377(4) | 0.9384(7) |
| H(13) | 0.244(9) | 0.229(10) | 0.105(22) |
| H(14) | 0.234(9) | 0.206(10) | 0.888(22) |
| H(22) | 0.435(11) | 0.270(10) | 0.330(20) |
| H(24) | 0.533(10) | 0.246(10) | 0.268(20) |
| H(32) | 0.419(9) | 0.234(9) | 0.664(21) |
| H(33) | 0.549(9) | 0.188(9) | 0.755(20) |
| H(41) | 0.632(10) | 0.055(11) | 0.212(21) |
| H(42) | 0.600(10) | 0.983(11) | 0.025(20) |
| H(54) | 0.356(10) | 0.906(10) | 0.961(18) |
| H(57) | 0.428(9) | 0.946(10) | 0.768(21) |
| H(65) | 0.281(11) | 0.033(11) | 0.320(20) |
| H(67) | 0.385(11) | 0.008(10) | 0.414(20) |
| H(71) | 0.431(10) | 0.492(11) | 0.975(20) |
| H(72) | 0.465(10) | 0.370(11) | 0.008(19) |

Table 2. MgSO₄·7H₂O, *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 $\frac{4}{3}(\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2)$

| Atom | β_{11} | β_{22} | β_{33} | β_{12} | β_{13} | β_{23} | B (Å ²) |
|-------|--------------|--------------|--------------|--------------|--------------|--------------|-----------------------|
| Mg | 0.0017(1) | 0.0021(1) | 0.0046(2) | 0.0002(1) | -0.0002(1) | 0.0001(1) | 1.00(5) |
| S | 0.0017(1) | 0.0022(1) | 0.0046(2) | -0.0003(1) | -0.0003(1) | -0.0001(1) | 1.00(5) |
| O(1) | 0.0068(4) | 0.0026(3) | 0.0135(9) | -0.0020(3) | -0.0023(5) | 0.0000(4) | 2.6(1) |
| O(2) | 0.0018(2) | 0.0057(3) | 0.0105(7) | 0.0004(2) | 0.0003(3) | 0.0011(5) | 2.1(1) |
| O(3) | 0.0029(2) | 0.0063(3) | 0.0070(6) | -0.0019(2) | 0.0013(3) | -0.0016(4) | 2.2(1) |
| O(4) | 0.0032(2) | 0.0031(2) | 0.0116(8) | 0.0003(2) | -0.0007(4) | 0.0018(4) | 1.9(1) |
| O(w1) | 0.0025(2) | 0.0051(3) | 0.0088(6) | 0.0016(2) | -0.0002(3) | -0.0007(4) | 2.0(1) |
| O(w2) | 0.0020(2) | 0.0034(3) | 0.0078(6) | -0.0003(2) | 0.0003(3) | -0.0016(3) | 1.5(1) |
| O(w3) | 0.0028(2) | 0.0047(3) | 0.0085(6) | -0.0001(2) | 0.0007(3) | 0.0025(4) | 2.0(1) |
| O(w4) | 0.0032(2) | 0.0050(3) | 0.0111(8) | 0.0027(2) | -0.0023(4) | -0.0025(4) | 2.3(1) |
| O(w5) | 0.0039(2) | 0.0029(2) | 0.0077(7) | -0.0005(2) | -0.0004(3) | -0.0010(3) | 1.8(1) |
| O(w6) | 0.0034(2) | 0.0047(3) | 0.0082(7) | -0.0003(2) | 0.0010(3) | 0.0025(4) | 2.1(1) |
| O(w7) | 0.0055(3) | 0.0035(3) | 0.0122(8) | 0.0004(2) | 0.0016(4) | 0.0007(4) | 2.5(1) |

Table 3. MgSO₄ · 7 H₂O, observed and calculated |F| multiplied by 10
Unobserved |F_o| marked by a minus sign

Table with 24 columns: H, K, L, OBS, CAL, H, K, L, OBS, CAL, H, K, L, OBS, CAL, H, K, L, OBS, CAL, H, K, L, OBS, CAL, H, K, L, OBS, CAL. It contains numerical data for various reflections, with unobserved values marked with a minus sign.

$e.\text{\AA}^{-3}$. The theoretical height of a hydrogen atom with a temperature factor of $B=3.0 \text{\AA}$ is $0.4 e.\text{\AA}^{-3}$, when the data are cut off at $\sin \theta/\lambda=0.36 \text{\AA}^{-1}$. The estimated standard deviation of the electron density, using Cruickshank's (1949) formula, is $0.08 e.\text{\AA}^{-3}$. This shows that the electron density peaks corresponding to the hydrogen atoms are significantly different from the background and moreover are approximately of the expected height. The highest 'ghost' has a density of $0.18 e.\text{\AA}^{-3}$. This is a rather high density compared with the lowest hydrogen atom peak and with the estimated standard deviation of ρ . The accuracy of the hydrogen positions therefore cannot be expected to be high, but the determined H positions make chemical sense.

In Tables 1 and 2 the final positional and thermal parameters which were used in calculating the F_c in Table 3 are presented. The B 's in Table 2 are the isotropic B 's equivalent to the anisotropic tempera-

Table 4. Interatomic distances and bond angles

(a) Coordination octahedron around Mg

| Distance | |
|-------------|------------|
| Mg-O(w1) | 2.054(4) Å |
| Mg-O(w2) | 2.099(4) |
| Mg-O(w3) | 2.045(4) |
| Mg-O(w4) | 2.046(4) |
| Mg-O(w5) | 2.092(4) |
| Mg-O(w6) | 2.055(4) |
| Mean value: | 2.065(2) Å |

| Distance | Angle |
|----------------|--------------|
| O(w1)-O(w2) | 2.924(5) Å |
| O(w1)-O(w3) | 2.864(5) |
| O(w1)-O(w4) | 4.099(5) |
| O(w1)-O(w5) | 2.973(6) |
| O(w1)-O(w6) | 2.832(6) |
| O(w2)-O(w3) | 3.005(6) |
| O(w2)-O(w4) | 2.878(5) |
| O(w2)-O(w5) | 4.191(5) |
| O(w2)-O(w6) | 2.940(6) |
| O(w3)-O(w4) | 2.898(6) |
| O(w3)-O(w5) | 2.890(6) |
| O(w3)-O(w6) | 4.096(5) |
| O(w4)-O(w5) | 2.951(6) |
| O(w4)-O(w6) | 3.003(6) |
| O(w5)-O(w6) | 2.893(6) |
| O(w1)-Mg-O(w2) | 89.5°(0.2°) |
| O(w1)-Mg-O(w3) | 88.6°(0.2°) |
| O(w1)-Mg-O(w4) | 177.1°(0.2°) |
| O(w1)-Mg-O(w5) | 91.6°(0.2°) |
| O(w1)-Mg-O(w6) | 87.1°(0.2°) |
| O(w2)-Mg-O(w3) | 92.9°(0.2°) |
| O(w2)-Mg-O(w4) | 87.9°(0.2°) |
| O(w2)-Mg-O(w5) | 178.1°(0.2°) |
| O(w2)-Mg-O(w6) | 90.1°(0.2°) |
| O(w3)-Mg-O(w4) | 90.2°(0.2°) |
| O(w3)-Mg-O(w5) | 88.6°(0.2°) |
| O(w3)-Mg-O(w6) | 174.8°(0.2°) |
| O(w4)-Mg-O(w5) | 91.0°(0.2°) |
| O(w4)-Mg-O(w6) | 94.2°(0.2°) |
| O(w5)-Mg-O(w6) | 88.5°(0.2°) |

(b) SO₄ tetrahedron

| Distance | |
|-------------|------------|
| S-O(1) | 1.460(4) Å |
| S-O(2) | 1.473(4) |
| S-O(3) | 1.469(4) |
| S-O(4) | 1.482(4) |
| Mean value: | 1.471(2) Å |

| Distance | Angle |
|-------------|--------------|
| O(1)-O(2) | 2.406(6) Å |
| O(1)-O(3) | 2.392(6) |
| O(1)-O(4) | 2.404(6) |
| O(2)-O(3) | 2.408(5) |
| O(2)-O(4) | 2.406(5) |
| O(3)-O(4) | 2.396(6) |
| O(1)-S-O(2) | 110.2°(0.3°) |
| O(1)-S-O(3) | 109.5°(0.3°) |
| O(1)-S-O(4) | 109.6°(0.3°) |
| O(2)-S-O(3) | 109.9°(0.2°) |
| O(2)-S-O(4) | 109.0°(0.2°) |
| O(3)-S-O(4) | 108.6°(0.3°) |
| Mean value: | 2.402(3) Å |
| Mean value: | 109.5°(0.1°) |

Table 4 (cont.)

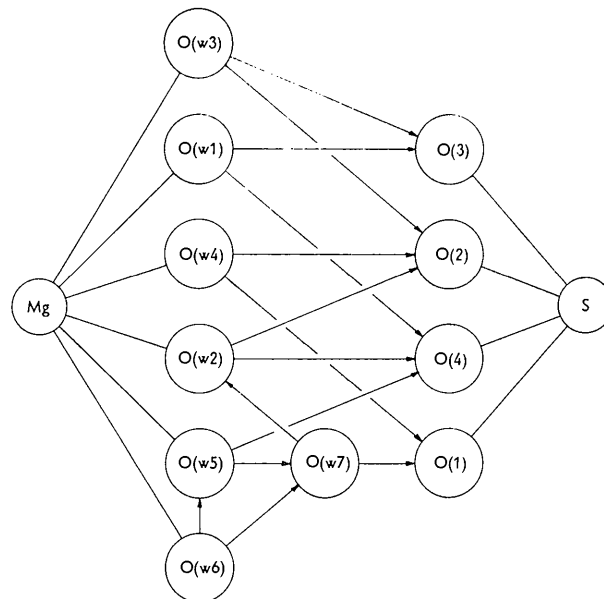
(c) Hydrogen bonds

| Distances | | Angle | |
|-------------|------------|-------------------|--------------|
| O(w1)-O(3) | 2.697(6) Å | O(3)-O(w1)-O(4) | 117.0°(0.2°) |
| O(w1)-O(4) | 2.769(6) | O(2)-O(w2)-O(4) | 97.1°(0.2°) |
| O(w2)-O(2) | 2.730(6) | O(2)-O(w3)-O(3) | 104.9°(0.2°) |
| O(w2)-O(4) | 2.733(5) | O(1)-O(w4)-O(2) | 101.2°(0.2°) |
| O(w3)-O(2) | 2.813(6) | O(4)-O(w5)-O(w7) | 121.7°(0.2°) |
| O(w3)-O(3) | 2.699(5) | O(w5)-O(w6)-O(w7) | 117.2°(0.2°) |
| O(w4)-O(1) | 2.716(6) | O(1)-O(w7)-O(w2) | 101.4°(0.2°) |
| O(w4)-O(2) | 2.978(6) | | |
| O(w5)-O(4) | 2.938(6) | Mean value: | 109° |
| O(w5)-O(w7) | 2.755(6) | | |
| O(w6)-O(w5) | 2.906(5) | | |
| O(w6)-O(w7) | 2.793(6) | | |
| O(w7)-O(1) | 2.821(6) | | |
| O(w7)-O(w2) | 2.906(7) | | |
| Mean value: | 2.80 Å | | |

(d) Water molecules

| Angle | Distances | | | |
|-------------------|---------------|---------------|------------|----------|
| | H-O(w) (Å) | O(w)-H (Å) | H-H (Å) | |
| H(13)-O(w1)-H(14) | 103°(12°) | 0.99(15) | 0.96(15) | 1.52(20) |
| H(22)-O(w2)-H(24) | 83°(12°) | 1.03(15) | 0.87(15) | 1.27(20) |
| H(32)-O(w3)-H(33) | 106°(12°) | 1.22(15) | 0.97(15) | 1.75(20) |
| H(41)-O(w4)-H(42) | 107°(12°) | 1.10(15) | 0.86(15) | 1.59(20) |
| H(54)-O(w5)-H(57) | 118°(12°) | 0.86(15) | 1.06(15) | 1.65(20) |
| H(65)-O(w6)-H(67) | 95°(12°) | 0.99(15) | 0.94(15) | 1.43(20) |
| H(71)-O(w7)-H(72) | 101°(12°) | 1.00(15) | 0.99(15) | 1.54(20) |
| Mean values: | 102°(5°) | 0.99(4) | 1.54(7) | |

ture factors according to the definition of Hamilton (1959). None of the thermal or positional parameters in Tables 1 and 2 are involved in high correlations. A minus sign on the F_o in Table 3 indicates that this reflection has not been observed. The F_o given here is equal to $|\frac{1}{2}.I_{\min}.Lp^{-1}|$ (Hamilton, 1955).

Fig. 1. MgSO₄ · 7H₂O, hydrogen bonding scheme.

The form factors used in calculating F_c were taken from *International Tables for X-ray Crystallography* (Ibers, 1962). The R value for 1845 F_{hkl} including the unobserved ones is 0.069.

Discussion of structure

The results of the refinement of orthorhombic $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ confirm fully the findings of Beavers & Schwartz (1935) for the isostructural $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ and are a tribute to the quality of this early work. The hydrogen bonding scheme shown in Fig. 1 had not to be changed; it is the same as proposed by

Beavers & Schwartz. Fig. 2 shows the details of the hydrogen bonding around the three different parts of the structure: the $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ octahedron, the SO_4^{2-} tetrahedron and O(w7), the water oxygen atom which is not coordinated to the magnesium ion.

The interatomic distances are given together with their estimated standard deviations in Table 4. The $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ polyhedron is, as usually in such hydrate structures, only approximately an octahedron. The deviations from cubic symmetry are not very large, but are significant. The O(w)-O(w) distances range from 2.83 to 3.01 Å, the 'right' angles O(w)-Mg-O(w) from 87 to 94°, the Mg-O(w) distances

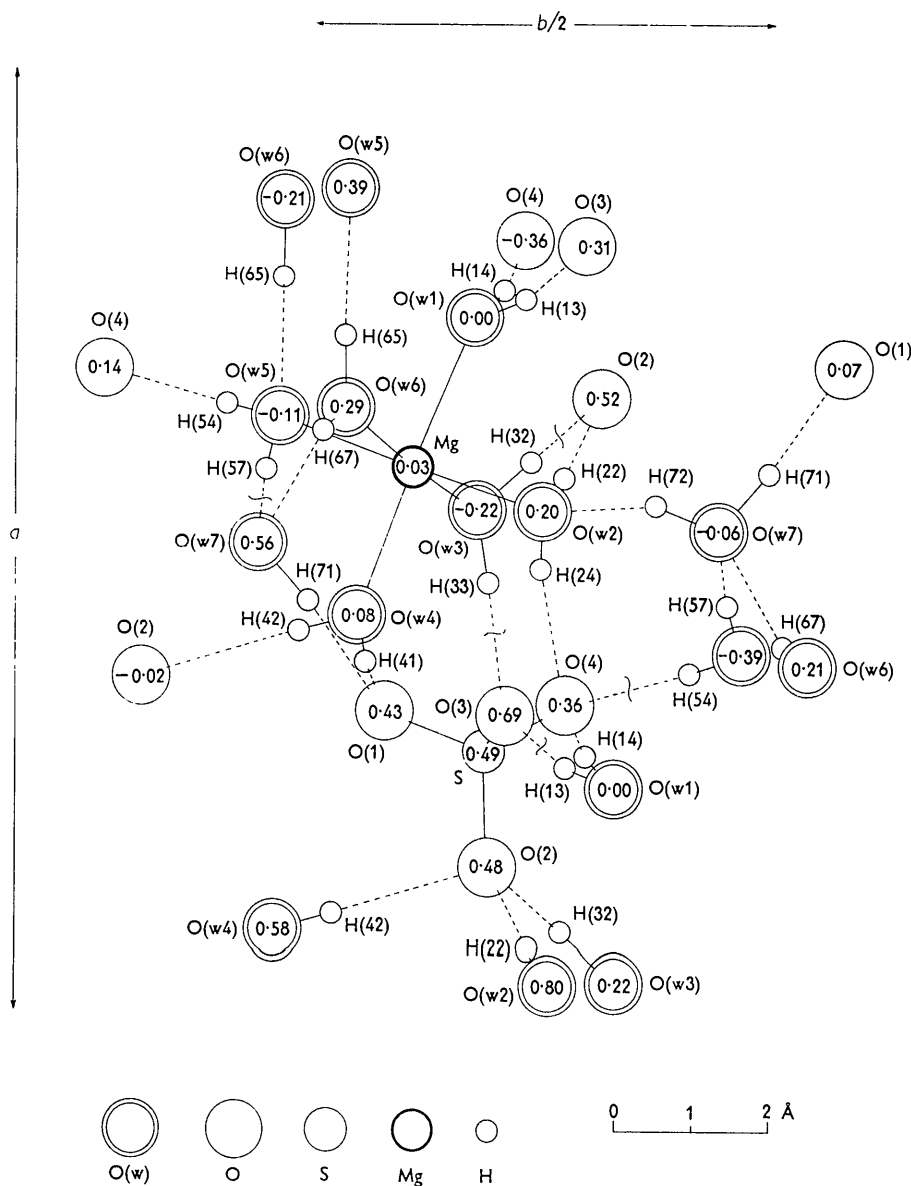


Fig. 2. $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, schematic projection parallel to $[001]$ illustrating the hydrogen bonding system. The numbers in the circles representing the atoms are the z parameters of these atoms.

Table 5. Comparison of S-O bond lengths in different crystal structures

| | Individual distances | | | | Mean value | Mean value after correction for thermal motion (in-phase) |
|---|----------------------|------------|------------|------------|------------|---|
| | S-O(1) | S-O(2) | S-O(3) | S-O(4) | | |
| Mg(NH ₄) ₂ (SO ₄) ₂ ·6H ₂ O ⁽¹⁾ | 1.459(5) Å | 1.474(5) Å | 1.481(5) Å | 1.476(5) Å | 1.473(2) Å | 1.486 Å |
| Li ₂ SO ₄ ·H ₂ O ⁽²⁾ | 1.462(2) | 1.479(2) | 1.482(2) | 1.466(2) | 1.472(1) | 1.480 |
| MgSO ₄ ·4H ₂ O ⁽³⁾ | 1.480(4) | 1.468(4) | 1.478(6) | 1.466(5) | 1.473(2) | 1.479 |
| FeSO ₄ ·7H ₂ O ⁽⁴⁾ | 1.488(4) | 1.481(4) | 1.466(4) | 1.462(4) | 1.474(2) | 1.485 |
| MgSO ₄ ·7H ₂ O ⁽⁵⁾ | 1.460(4) | 1.473(4) | 1.469(4) | 1.482(4) | 1.471(2) | 1.486 |
| Average of the mean values: | | | | | 1.473(1) Å | |

(1) Margulis & Templeton, 1962.

(2) Larson, 1963.

(3) Baur, 1964a.

(4) Baur, 1964b.

(5) This work.

from 2.04₅ to 2.09₉ Å. The mean of the two longer bonds from Mg to O(w2) and O(w5) is 2.09₆ Å, the mean of the other four ones is 2.05₀ Å. The difference is highly significant. O(w2) and O(w5) are the two water oxygen atoms which act as acceptor atoms to hydrogen bonds from O(w7) and O(w6). The sum of the electrostatic bonds (Pauling, 1960) which they receive is thus higher than for the remaining water oxygens which are bonded to Mg²⁺ only. In order to achieve an effective balance of the electrostatic valences with the sum of the electrostatic bonds for the water oxygen atoms O(w2) and O(w5), the distances Mg-O(w) are lengthened for these two bonds. Further examples of such lengthening (and shortening) of bonds may be found in paper I of this series (Baur, 1962) and in Baur (1961). The mean value of all six Mg-O(w) bonds is 2.06₅ Å. This value is similar to the corresponding mean bond length of 2.06₉ Å in Mg(NH₄)₂(SO₄)₂·6H₂O (Margulis & Templeton, 1963) and to the mean Mg-O(w) bond length of 2.07₁ Å in MgSO₄·4H₂O (II = Baur, 1964a). The fact that the mean value of the bond length is not affected by the lengthening of Mg-O(w2) and Mg-O(w5) calls for an explanation. Apparently the distances between Mg²⁺ and O(w) represent an equilibrium position not only between Mg²⁺ and O(w), but between Mg²⁺ and the different water oxygen atoms themselves as well. When, as in the present case, two Mg-O(w) distances are somewhat larger than the other ones, the remaining ligands find energetically more favorable positions nearer to the cation, since the electrostatic repulsion from the two ligands which moved outward is lessened. The analogous effect can be observed in FeSO₄·7H₂O (III), where in the coordination octahedron around Fe(2) the two distances Fe(2)-O(w6) are lengthened to 2.19 Å because of outward hydrogen bonding; correspondingly Fe(2)-O(w4) and Fe(2)-O(w5) are shortened to 2.10 Å. The mean Fe(2)-O(w) distance is 2.13 Å, essentially the same distance as in FeSO₄·4H₂O (I), where it is 2.12 Å.

During the last few years a number of high precision determinations of crystal structures of sulfates have been made. The results for the sulfate group agree remarkably well (Table 5). The mean values of the

S-O bond length in these five compounds are with n 0.003 Å the same. The individual bond length, however, spread from 1.459 to 1.488 Å. Many of these individual bond lengths are possibly significantly different from their mean values. The mean values of the angle O-S-O are identical with the tetrahedral angle, while the individual angles vary from 108.4° to 112.0°; these differences, and the differences between the individual O-O distances (range: 2.387–2.433 Å) within the tetrahedral group are significant. It seems that the shape of the sulfate group is very near to an ideally tetrahedral configuration, but that the small deviations from this shape are distinct. They may be connected with the differences in environment of the individual oxygen atoms: the 6 sulfate oxygen atoms which receive a sum of electrostatic bonds between 0.33 and 0.42 have an average S-O bond length of 1.464 Å, the remaining 14 sulfate oxygen atoms have an average of 1.476 Å and the sum of electrostatic bonds which they receive is 0.50 to 0.67 (one hydrogen bond is counted as 0.166, see I).

The average hydrogen bonding distance O(w)-O is 2.80 Å, the individual values range from 2.70 to 2.98 Å. The angles O-O(w)-O spread from 97° to 122°, the average being 109°. The hydrogen positions are near the connecting lines of the water oxygen atoms and the acceptor atoms of the hydrogen bond, at an average distance from the acceptor atom of 1.8 Å, the individual distances ranging from 1.6 to 2.1 Å. The angles O(w)-H-O spread from 145° to 178°, having a mean value of 168°. Surprisingly the mean values (Table 4(d)) of the angle H-O(w)-H, and the distances O-H and H-H are close to the values to be expected for the shape of the water molecule from neutron diffraction studies: in MgSO₄·4H₂O (II) the averaged results for four different H₂O molecules are ∠ H-O-H 109.6°, distance O-H 0.967 Å, distance H-H 1.575 Å. The deviations from these values found here are in all but one case (∠ H(22)-O(w2)-H(24)) not significant. The scatter around the mean values does not show any unexpected trends. In view of the consistency of the results for the shape of the water molecule as determined by neutron diffraction and

by nuclear magnetic resonance methods for a number of salt hydrates it seems reasonable to assume that the water molecule in $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ has the same shape as, say in $\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$ (II) (for a review of the literature on hydrogen positions in crystals compare Hamilton, 1962, and McGrath & Silvidi, 1961). It can be concluded then, that within the limits of accuracy of the present investigation the location of the nucleus of the hydrogen atom in the water molecule (as determined by neutron diffraction) is the same as the center of the electron density cloud of the hydrogen atom (as determined by X-ray diffraction).

$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ cleaves perfectly along (010). This cleavage is in agreement with the hydrogen bonding system as described here. In order to cleave the crystal along (010), 8 hydrogen bonds have to be broken per unit cell, namely O(w4)–O(2), O(w5)–O(4), O(w6)–O(w5) and O(w7)–O(w2), each twice. These four bonds are the longest hydrogen bonds in the structure, their mean length being 2.93 Å, as opposed to an average of 2.75 Å for the ten remaining ones. These 10 stronger bonds connect the $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ octahedra with the SO_4^{2-} tetrahedra and O(w7) to form a puckered layer parallel to (010). For cleavage along other planes these stronger bonds would have to be disrupted; for instance parallel to (100) 8 of the shorter and 4 of the longer bonds per unit cell had to be cut to cleave the crystal.

Table 6. $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, root-mean-square thermal displacements along principal axes

| Atom | Axis 1 | Axis 2 | Axis 3 |
|-------|------------|------------|------------|
| Mg | 0.101(3) Å | 0.110(3) Å | 0.127(3) Å |
| S | 0.100(2) | 0.111(2) | 0.131(2) |
| O(1) | 0.112(8) | 0.173(6) | 0.240(6) |
| O(2) | 0.110(6) | 0.155(6) | 0.207(6) |
| O(3) | 0.113(7) | 0.131(6) | 0.233(6) |
| O(4) | 0.125(7) | 0.157(6) | 0.183(6) |
| O(w1) | 0.113(6) | 0.144(5) | 0.209(5) |
| O(w2) | 0.119(6) | 0.119(6) | 0.172(6) |
| O(w3) | 0.116(7) | 0.147(6) | 0.199(6) |
| O(w4) | 0.095(8) | 0.143(6) | 0.239(6) |
| O(w5) | 0.120(7) | 0.153(6) | 0.172(5) |
| O(w6) | 0.112(7) | 0.163(6) | 0.199(6) |
| O(w7) | 0.155(7) | 0.164(7) | 0.209(6) |

The average of the angles between the axis of maximum displacement (Axis 3, Table 6) of O(w) and O with the lines connecting them to Mg and S respectively are $85^\circ(2^\circ)$ and $84^\circ(2^\circ)$; the intermediate axis (2) encloses angles of $88^\circ(3^\circ)$ and $89^\circ(4^\circ)$, the short axis (1) $170^\circ(3^\circ)$ and $173^\circ(3^\circ)$ with these lines. Since the root-mean-square thermal displacements along the short axes of O(w) and O are of approximately the same magnitude as those of Mg and S respectively, while they are significantly larger in their long axes, this thermal motion may be explained

by an oscillation of the whole groups as rigid bodies. Assuming such angular oscillation of the sulfate group and the $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ octahedron the corrections to the Mg–O(w) and S–O distances have been computed (Busing & Levy, 1957). The mean Mg–O(w) bond length after the in-phase correction (assuming O(w) to 'ride' thermally on Mg) is 2.074 Å compared with 2.065 Å without the correction. For the mean S–O bond length the value after applying the in-phase correction is 1.486 Å. After correction for thermal motion the mean values for the S–O bond length of the five compounds listed in Table 5 do not agree so well as without this correction; however if the three compounds are compared in which the sulfate oxygen atoms are only hydrogen bonded, the agreement is even better. This could mean that either the distances are really different, or (what is more probable) that the simplifying assumption of rigid body motion does not hold for $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ and $\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$, since in both these compounds the sulfate oxygen atoms belong to the coordination polyhedron around the cation and the thermal motion of the sulfate oxygen atoms is more complex.

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Trioctahedral One-Layer Micas. I. Crystal Structure of a Synthetic Iron Mica*

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The structure of a synthetic iron mica, $\text{KFe}_3^{2+}(\text{Fe}^{3+}\text{Si}_3)\text{O}_{10}(\text{OH})_2$, determined from visually estimated intensities, shows very slight departure from Pabst's idealized biotite structure. The sextuple cell formerly used to describe micas accounts for the observed twinning.

Introduction

The structure determination of synthetic‡ iron mica, 'ferri-annite', $\text{KFe}_3^{2+}(\text{Fe}^{3+}\text{Si}_3)\text{O}_{10}(\text{OH})_2$, was begun (Donnay & Kingman, 1958) at a time when no refined structural data were available for any member of the mica group. To understand the polymorphism of mica, it seemed essential to collect, as accurately as possible, bond lengths and angles for samples of known compositions. For that reason we began our study with an unusual synthetic mica, of relatively simple formula, prepared by Wones (1958) at the Geophysical Laboratory.

In the meantime crystal structures of four natural micas have been published. Xanthophyllite, $\text{Ca}_{1.10}\text{Mg}_{2.18}\text{Al}_{0.72}(\text{Al}_{2.95}\text{Si}_{1.05})\text{O}_{10}(\text{OH})_2$, a trioctahedral, brittle mica of type $1M$ (Smith & Yoder, 1956), was analyzed by Takéuchi & Sadanaga (1959). Radoslovich (1960) refined the dioctahedral $2M_1$ muscovite, $\text{KAl}_2(\text{AlSi}_3)\text{O}_{10}(\text{OH})_2$. Zvyagin & Mishchenko (1962), by electron diffraction, studied a trioctahedral $1M$ mica, $\text{KMg}_3(\text{AlSi}_3)\text{O}_{10}(\text{OH})_2$. An iron-rich phlogopite, $(\text{K}_{0.9}\text{Mn}_{0.1})\text{Mg}_3[(\text{Fe}^{3+}, \text{Mn})\text{Si}_3]\text{O}_{10}(\text{OH})_2$, of type $1M$ was refined by Steinfink (1962). Apart from a slight substitution of Mn for K and Fe^{3+} , this last mica

differs from our ferri-annite only in the octahedral layer, which is occupied by Mg instead of Fe^{2+} .

The reader will be able to compare ferri-annite with these four recent structures in the light of recent theoretical discussions by Radoslovich (1959, 1961, 1962, 1963*a-c*) and Radoslovich & Norrish (1962). The crystallochemical implications of our results will be considered in a forthcoming paper.

Experimental

The crystals were prepared by Wones (1958, 1963), who reports on his synthesis as follows: *The crystals formed on the gas-liquid interface of a run containing gas, liquid, wüstite, and fayalite during a slow quench from 850 °C at 2070 bars total pressure. The optical properties and powder data of these relatively large crystals are identical with those of smaller crystals formed in runs of ferri-annite composition that gave 100% yield. The weight proportions of the constituents in these runs are known with 2% accuracy, and the composition of the crystals used in this study is estimated to be known with the same accuracy.* The crystals are black, euhedral, platy parallel to (001) and up to 1 mm in thickness. Their (001) cleavage is perfect. Twinning is frequent.

Cell dimensions, determined by single-crystal methods,* are: $a=5.43$, $b=9.40$, $c=10.32$ Å, all three

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‡ Because this composition has not been found in nature, it would be better not to designate it by a mineral name. This is the reason for the quotation marks that enclose ferri-annite, the first time the name appears in the text.

* The cell dimensions have since been refined by Wones (1963) from powder data by least squares: $a=5.430 \pm 0.002$, $b=9.404 \pm 0.005$, $c=10.341 \pm 0.003$, $\beta=100^\circ 4' \pm 10'$. The cell volume is 519.9 \AA^3 and the calculated density is 3.45 g.cm^{-3} .