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# The crystal structure of hohmannite, $Fe_2(H_2O)_4[(SO_4)_2O].4H_2O$ and its relationship to amarantite, $Fe_2(H_2O)_4[(SO_4)_2O].3H_2O$

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HOHMANNITE is a hydrated sulphate of ferric iron with the formula $Fe_2(SO_4)_2(OH)_2.7H_2O$ (Palache, Berman, and Frondel, 1951).

Figs. 1 and 2 illustrate the structure of hohmannite. The first shows a complex chain of Fe(O, $H_2O)_6$ octahedra and $SO_4$ tetrahedra, which runs along the *c* axis; the second visualizes the water molecules and an hypothetical hydrogen-bonds system obtained on the basis of electrostatic and geometrical considerations.

Except for the hydroxyl groups, the structure results agree with the composition mentioned above. In fact, according to the hydrogen bonds system shown in fig. 2, no hydroxyl group exists, consequently the chemical formula $Fe_2(H_2O)_4[(SO_4)_2O].4H_2O$ seems more reliable.

In hohmannite there are two Fe(O, $H_2O)_6$ octahedra, two $SO_4$ tetrahedra, four coordinating and four structural waters crystallographically independent. Both Fe(1) and Fe(2) exibite a distorted octahedral coordination with cation–anion distances ranging from 1·93 to 2·06 Å and 1·87 to 2·10 Å respectively. Fe(1) is surrounded by five oxygens and one water molecule, Fe(2) by three oxygens and three waters. The two $SO_4$ groups have both three longer and one shorter distances. Two centrosymmetrical pairs of Fe(O, $H_2O)_6$ octahedra and $SO_4$ tetrahedra are linked together to form a group of composition $[Fe_4(H_2O)_4O_8(SO_4)_4]^{12-}$. These groups polymerize via O(8) to form chains of Fe–O–S linkages along *c*. Coordinating and structural water molecules provide the hydrogen bond system to connect these chains.

Taking into account the linkages between $Fe^{3+}$(O, OH, $H_2O)_6$ octahedra and $SO_4$ tetrahedra Süsse (1971) gives a crystal-chemical classification of some natural ferrisulphates. According to this classification hohmannite, like amarantite, belongs to the second type of the three quoted, i.e. infinite chains of Fe–O–S linkages.

Hohmannite, $Fe_2(H_2O)_4[(SO_4)_2O].4H_2O$, is in effect a higher hydrate of amarantite, $Fe_2(H_2O)_4[(SO_4)_2O].3H_2O$, and has been obtained from amarantite by a partial dehydration followed by a successive rehydration (Césbron, 1964). The solution of the structure of hohmannite permits a useful comparison with the structure of amarantite (Süsse, 1968; Giacovazzo and Menchetti, 1969). Both these minerals have the same $P\bar{1}$ space group, comparable reticular parameters, and differ chemically only by the water content. This last difference affects the orientation of the chains' repeat unit $[Fe_4(H_2O)_4O_8(SO_4)_4]^{12-}$ and the hydrogen bond system. In fact owing to the greater number of water molecules in hohmannite, these units under-go some modification, of which the more important is a rotation of about 50°. The consequence of this is the breakage of the hydrogen bond system of amarantite and the building of a new one in hohmannite.

Scharizer (1927) and Césbron (1964) give for hohmannite and amarantite comparable TGA curves, in agreement with the structural results. The only difference in these curves is that hohmannite starts dehydration at normal temperature, amarantite from 60 °C onwards. The structural explanation is that O(17)w forms the weaker hydrogen bonds and, of course, has the higher temperature factor. So this water seems to be the first to be lost by hohmannite in the reaction amarantite $+ 1H_2O \rightleftharpoons$ hohmannite.

The structure of hohmannite accounts for some physical properties, as a higher refractive index compared with amarantite, the elongation on the [001] direction and cleavage on {010}, {1$\bar{1}$0}, and {110} quoted in Dana's System of Mineralogy and on {100} (not quoted).

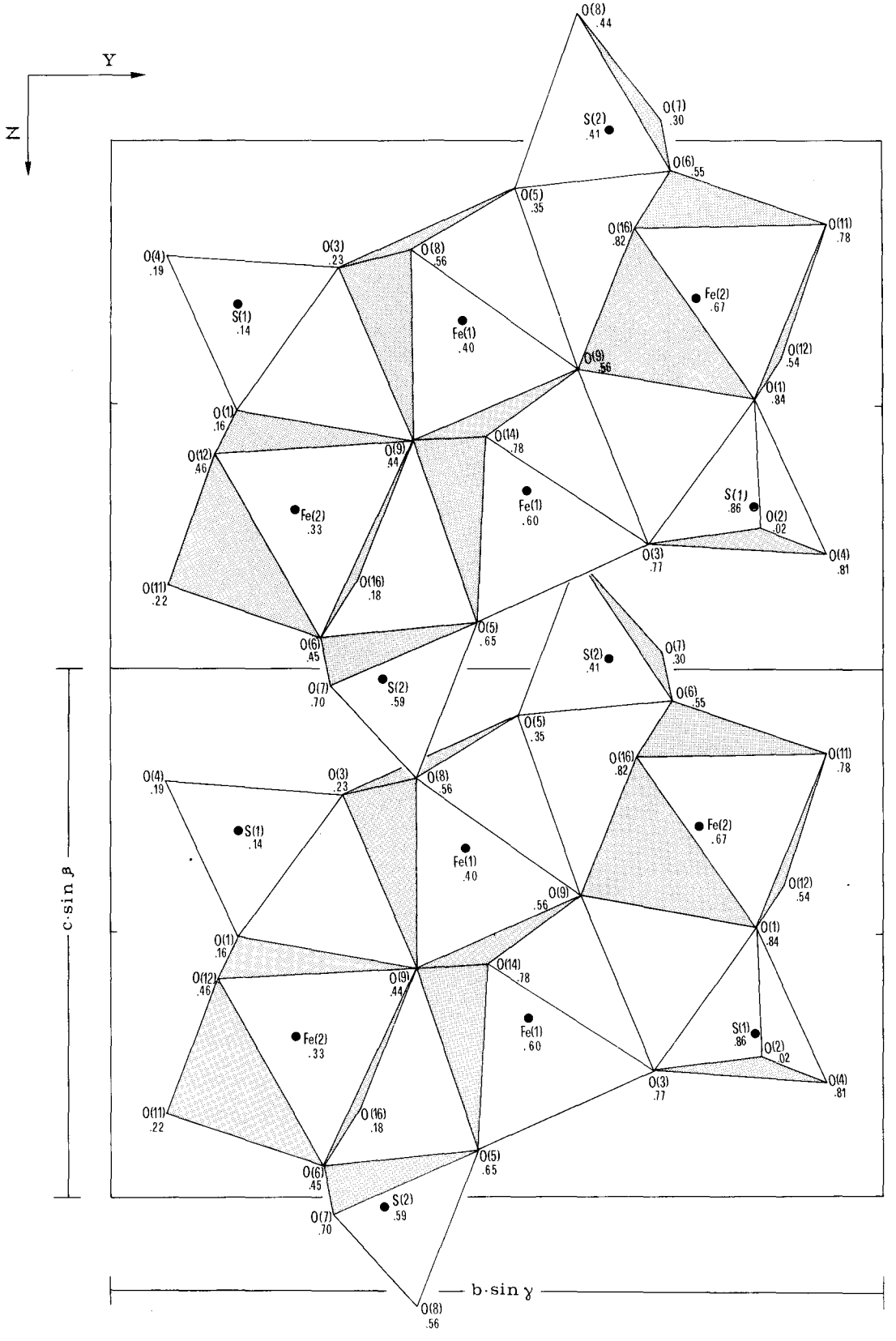


FIG. 1. Chain of Fe–O–S linkages running along the $c$-axis. Next to each atom is given its $x$ coordinate.

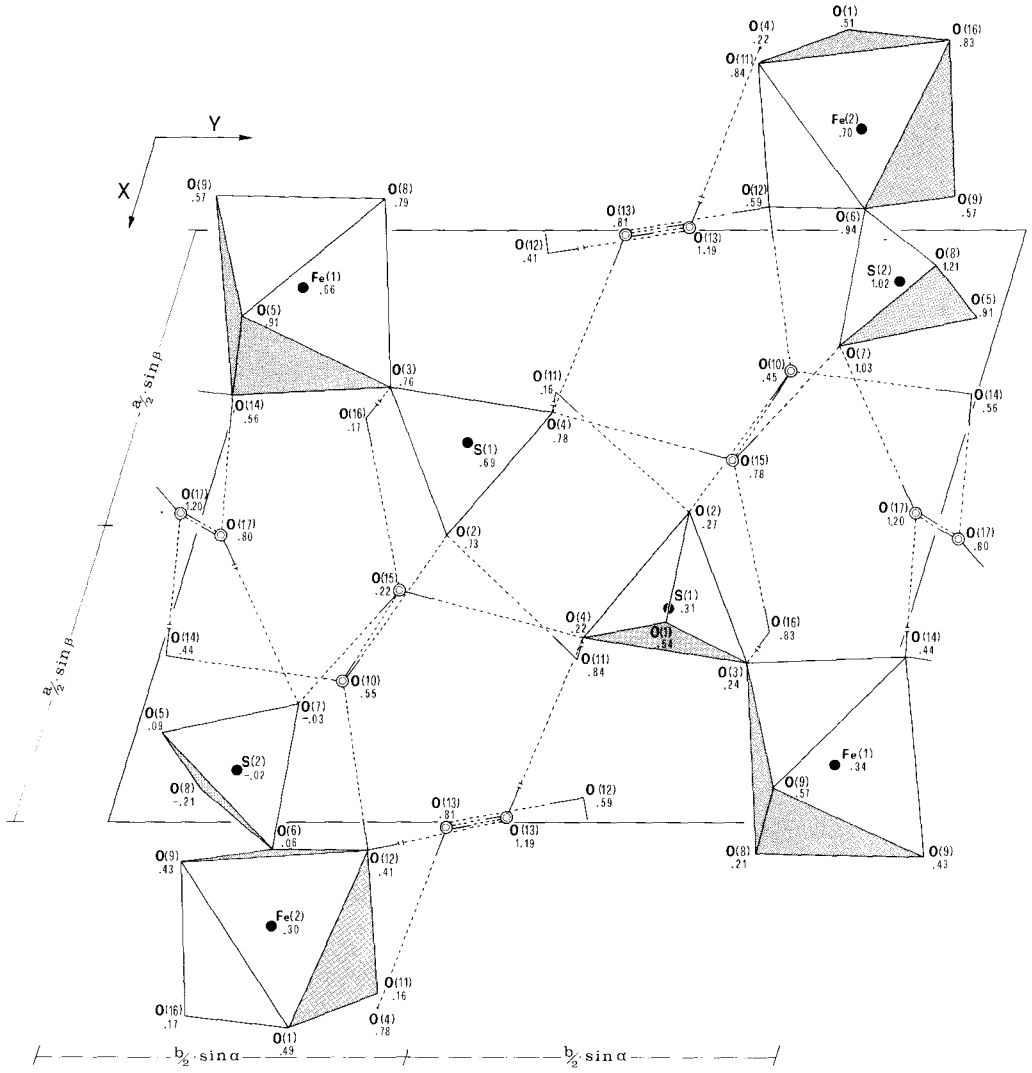


FIG. 2. The crystal structure of hohmannite showing the water molecules and the probable hydrogen-bond system. Next to each atom is given its $z$ coordinate.

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THE CRYSTAL STRUCTURE OF HOHMANNITE, $Fe_2(H_2O)_4[(SO_4)_2C].4H_2O$ AND ITS RELATIONSHIP TO AMARANTITE, $Fe_2(H_2O)_4[(SO_4)_2C].3H_2O$.

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Hohmannite is a hydrated sulphate of ferric iron with the formula $Fe_2(SO_4)_2(OH)_2.7H_2O$ according to Palache, Berman, and Frondel (1951) and to Strunz (1970). The composition of the mineral has been verified by several authors, who give comparable analyses. It has been found associated with other secondary sulphates in desert areas.

Hohmannite was mistaken for amarantite by Frenzel, who first described it in 1887, according to Cesbron (1964). Darapsky (1890) and Rogers (1931) studied as castanite a mineral that Unce-ach (1935) showed to be hohmannite. The 'castanite' of Bandy (1938) has indices of refraction very near to those given later by the same author for hohmannite (Bandy, 1938). Cesbron (1964) found hohmannite to be triclinic, with a 9.05(2), b 10.88(2), c 7.47(2) Å, $\alpha$ 90°0', $\beta$ 90°35', $\gamma$ 106°58', and Z=2. The determination of the crystal structure of hohmannite allows a useful comparison to be made with the structure of amarantite, already determined by Süsse (1968) and by Giacovazzo and Menchetti (1969). The small difference between the structures accounts for some physical analogies that characterize these two minerals.

Esperimental. The crystal employed in this study is from a sample from Sierra Gorda, Chile, kindly supplied by Dr Cesbron. Before starting to measure the intensities it was lacquered to prevent dehydration as much as possible. A small prismatic crystal was investigated by Weissenberg photography to verify the symmetry. According to Cesbron (1964) it is triclinic, and both P1 and $P\bar{1}$ were possible; however, a piezoelectric test showed P1 to be more reliable.

The lattice parameters of hohmannite were refined by the least-squares method applied to 22 accurately indexed reflections from an X-ray powder pattern. Crystal data are: a 9.148(1), b 10.922(1), c 7.183(3) Å, $\alpha$ 90.29(6)°, $\beta$ 90.79(4)°, $\gamma$ 107.36(2)°, $\mu_{1.0-K\alpha}$ 25.1 $cm^{-1}$ $\mu_{Rmax.}$ 0.6, V 684.9 $Å^3$, Z 2, $\rho_{meas.}$ 2.255 $g.cm^{-3}$, $\rho_{calc.}$ 2.250 $g.cm^{-3}$

Intensities were collected by means of a Phillips PW 1100 four-circle automatic diffractometer (Centro di Cristallografia Strutturale del C.N.R., Pavia, Italy) with Mo radiation employing $\omega$-2$\theta$ scan technique. The scan rate was 0.04°/sec and the scan range 2°. Within a 2$\theta$ range of 50° a total of 2411 reflections were collected, of wh ch 1807 with $I > 3\sigma(I)$ were used in the refinement. The intensities were corrected for Lorentz effect and polarization but not for the absorption effect.

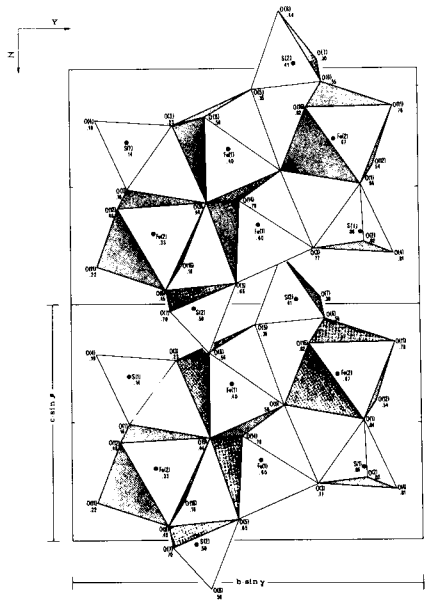


Fig. 1. Chain of Fe-O-S linkages running along the c axis. Next to each atom is given its x coordinate.

TABLE 1. Fractional atomic coordinates, anisotropic temperature factors ($x10^3$), and equivalent temperature factors according to Hamilton (1959). Standard deviations are in parentheses.

| Atom | x | y | z | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ | $B_H$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Fe(1) | 0.4022(1) | 0.4571(1) | 0.3384(1) | 4.8(1) | 2.2(1) | 2.8(1) | 0.3(1) | 0.5(1) | -0.7(1) | 0.9 |
| Fe(2) | 0.6693(1) | 0.7607(1) | 0.3044(1) | 5.5(1) | 2.3(1) | 2.9(2) | 0.0(1) | 0.9(1) | -0.4(1) | 1.0 |
| S(1) | 0.1399(2) | 0.1742(1) | 0.3089(2) | 5.6(2) | 2.7(1) | 4.0(3) | 0.1(1) | 0.4(2) | -0.9(1) | 1.0 |
| S(2) | 0.5915(2) | 0.3543(1) | 0.0194(2) | 5.2(2) | 2.5(1) | 3.0(3) | 0.9(1) | 0.9(2) | -0.5(1) | 0.9 |
| O(1) | 0.1645(5) | 0.1685(4) | 0.5126(6) | 7.3(7) | 5.5(4) | 3.7(9) | -0.9(4) | -0.1(6) | 0.0(5) | 1.8 |
| O(2) | -0.0193(5) | 0.1574(4) | 0.2700(6) | 6.3(7) | 5.2(5) | 10.9(10) | 0.4(4) | -0.1(6) | -1.4(5) | 1.5 |
| O(3) | 0.2334(5) | 0.3017(4) | 0.2431(6) | 8.0(6) | 3.6(4) | 4.2(9) | -0.1(4) | 1.1(6) | -0.2(5) | 1.5 |
| O(4) | 0.1929(5) | 0.0750(4) | 0.2173(6) | 13.0(7) | 3.3(5) | 8.4(10) | 2.4(5) | 2.9(6) | -1.7(5) | 1.8 |
| O(5) | 0.3531(5) | 0.5279(4) | 0.0900(6) | 7.9(6) | 4.2(4) | 5.5(9) | -0.8(4) | -0.8(6) | 0.9(5) | 1.6 |
| O(6) | 0.5523(5) | 0.7270(4) | 0.0634(6) | 8.5(6) | 3.7(4) | 4.4(9) | -0.8(4) | 0.0(6) | -0.2(5) | 1.6 |
| O(7) | 0.7045(5) | 0.2876(4) | 0.0300(6) | 11.6(7) | 6.7(5) | 6.5(10) | 5.6(4) | 1.1(6) | -0.7(5) | 1.9 |
| O(8) | 0.5600(5) | 0.3901(4) | 0.2093(6) | 7.7(6) | 5.5(4) | 2.6(9) | 2.7(4) | 1.1(6) | -1.6(5) | 1.5 |
| O(9) | 0.5568(4) | 0.6123(4) | 0.4259(5) | 5.2(5) | 2.3(4) | 2.8(8) | 0.0(4) | 0.4(5) | -0.6(4) | 0.9 |
| O(10)w | 0.7442(7) | 0.2428(6) | 0.4473(8) | 13.8(9) | 7.4(6) | 23.0(13) | 3.2(6) | 6.4(9) | -0.8(7) | 2.5 |
| O(11)w | 0.7797(5) | 0.9303(4) | 0.1632(6) | 11.6(6) | 4.2(4) | 3.3(9) | -1.1(4) | 1.3(6) | 0.1(5) | 2.0 |
| O(12)w | 0.5379(5) | 0.8648(4) | 0.4061(6) | 10.4(7) | 4.2(5) | 10.1(10) | 3.2(5) | 3.5(6) | 0.1(5) | 1.6 |
| O(13)w | 0.4877(6) | 0.0406(5) | 0.1892(8) | 15.3(9) | 8.0(6) | 14.4(12) | 6.1(6) | 3.4(8) | 2.5(7) | 2.5 |
| O(14)w | 0.2234(5) | 0.5126(4) | 0.4426(6) | 5.7(7) | 5.8(5) | 12.1(9) | 2.4(4) | 1.4(6) | -2.4(5) | 1.4 |
| O(15)w | 0.1128(6) | 0.8051(5) | 0.2167(7) | 9.7(8) | 6.4(6) | 19.3(12) | 2.6(5) | 3.6(8) | -2.1(6) | 1.9 |
| O(16)w | 0.8182(5) | 0.6790(4) | 0.1751(6) | 8.5(7) | 5.9(5) | 9.9(10) | 2.3(5) | 1.6(6) | -2.8(5) | 1.7 |
| O(17)w | 0.9839(8) | 0.4732(7) | 0.2052(10) | 12.3(12) | 13.5(9) | 32.1(18) | 3.0(8) | -4.4(12) | -1.0(10) | 3.3 |

Solution of the structure and refinement. The space group P1 was initially chosen and later confirmed by the crystal structure success. Some preliminary considerations were useful: Hohmannite and amarantite are two very closely related minerals, and similarities such as chemical formulae, lattice constants, space groups, and thermal data seemed to indicate that the structural units of tetrahedra and octahedra present in amarantite were probably also present in hohmannite. The positions of two crystallographically independent iron and two sulphur atoms were determined with the aid of three-dimensional Patterson syntheses. Subsequent structure-factor calculations and Fourier syntheses led to the determination of the positions of all 21 independent non-hydrogen atoms.

The refinement of the parameters was carried out by a full-matrix least-squares method using the program CAFLS (Busing, Martin, and Levy, (1962). The atomic-scattering curves were prepared from the values given in the International Tables (1962). All reflections were given unit weight. At the end of the refinement, including scale factor, positional parameters, and thermal factors, the R value was 0.075 for the isotropic temperature-factor mode, and 0.039 in the anisotropic one

Table II. Bond distances involving Fe-O and S-O atoms in hohmannite and amarantite (Süsse, 1968), with their standard deviations

| | Hohmannite | Amarantite | | Hohmannite | Amarantite |
|---|---|---|---|---|---|
| Fe(1)-O(3) | 2.032(4)Å | 2.042(6)Å | Fe(2)-O(10)w | 2.066(5)Å | 2.069(6)Å |
| -O(5) | 2.045(4) | 2.055(6) | | | |
| -O(8) | 2.034(4) | 2.045(6) | S(1)-O(1) | 1.481(5) | 1.496(6) |
| -O(9) | 1.943(4) | 1.923(6) | -O(2) | 1.439(5) | 1.456(6) |
| -O($\bar{1}$) | 1.935(4) | 1.969(6) | -O(3) | 1.493(4) | 1.495(6) |
| -O(14)w | 2.056(5) | 2.071(6) | -O(4) | 1.469(5) | 1.456(6) |
| Fe(2)-O(1) | 1.967(4) | 1.986(6) | S(2)-O(5) | 1.470(5) | 1.489(6) |
| -O(6) | 1.995(4) | 2.026(6) | -O(6) | 1.468(4) | 1.495(6) |
| -O(9) | 1.970(4) | 1.992(6) | -O(7) | 1.433(5) | 1.439(6) |
| -O(11)w | 2.100(5) | 2.074(6) | -O(8) | 1.473(4) | 1.489(6) |
| -O(12)w | 2.025(5) | 2.052(6) | w: Oxygen of water molecules | | |

Atomic coordinates and temperature factors are listed in Table I. A table containing observed and calculated structure factors is deposited in the library of the Dept.of Mineralogy, British Museum (Natural History), from which copies may be purchased.

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Structure analysis. Schematic and partial views of the structure of hohmannite are shown in figs. 1 and 2. The first represents a structural unit that is the skeleton of the structure, while the second visualizes the water molecules and their function in connecting similar units like that illustrated in fig.1. For ease of comparison, the sketches and designations accepted for hohmannite conform with those used by Süsse (1966) for amarantite.

The two crystallographically independent Fe atoms are surrounded octahedrally by oxygen atoms. Some of these are water molecules, which in the Tables are indicated by w. The individual ranges of Fe(1)-O and Fe(2)-O distances lie between 1.92 and 2.06 Å and between 1.87 and 2.10 Å respectively. Both ranges agree with those found in amarantite, which are 1.92 to 2.09 Å for Fe(1)-O and 1.89 to 2.07 Å for Fe(2)-O. For fuller details see Tables II and III, in which there is a systematic comparison of the distances and angles of equivalent polyhedra in the two minerals.

In hohmannite there are two $SO_4$ groups symmetrically unrelated. However, both have three longer and one shorter distance, whereas in amarantite the S(1) tetrahedron has two longer and two shorter distances (Table II). These differences can be partly explained on the basis of the proposed hydrogen-bond system for hohmannite (fig.2). In fact, O(4) appears to be linked by hydrogen bonds to three water molecules in hohmannite, in amarantite only to two (fig.6). Another difference between the structures of the two minerals concerns the angles and the cation-anion distances as a whole; the modifications involving angles and distances are directly connected with the two additional water molecules in the unit cell of hohmannite. As regards the angles we may note that those related to Fe atoms are more affected than those related to S atoms (Table III). The weighted mean values of the cation-anion distances, $\overline{Fe(1)-O}$ 2.007(4), $\overline{Fe(2)-O}$ 1.997(5), $\overline{S(1)-O}$ 1.468(5), and $\overline{S(2)-O}$ 1.462(5) in hohmannite, are all shorter than the corresponding distances in amarantite, $\overline{Fe(1)-O}$ 2.026(6), $\overline{Fe(2)-O}$ 2.011(6), $\overline{S(1)-O}$ and $\overline{S(2)-O}$ 1.478(6) Å. This small but significant difference (with the exception of S(1)-O owing to the S(1)-O(4) distance) can be ascribed to the higher density of hohmannite (2.25 $g.cm^{-3}$) compared with that of amarantite (2.14 $g.cm^{-3}$). Also an analysis of the atomic density carried out around Fe and S polyhedra shows a greater crowding of first neighbour oxygen atoms in hohmannite.

As in amarantite two centrosymmetrical pairs of octahedra and tetrahedra are connected to form a group of composition $Fe_4(H_2O)_4O_8(SO_4)_4$ as shown in fig.3. Such groups sharing O(8) polymerize to form chains of Fe-O-S linkages along c. The connections between these chains form a complex system of hydrogen bond. This system could not be resolved directly by a difference Fourier synthesis but only by the agreement of the electrostatic valency balance and geometric criteria (Tables IV, V, and VI); moreover, the scheme illustrated in fig.4

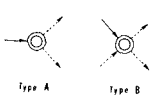


Fig.4. Sketches of two possible types of water molecules (double circles) linked to a trivalent cation (modified from Evans, 1964). In the structure of hohmannite only the A-type is present, as in the structure of amarantite. The unbroken arrows indicate the Fe-O bonds, the broken ones the H-O bonds.

agrees with the behaviour of the hydrogen-bond system in amarantite (fig.5) - i.e. the water molecules linked to $Fe^{3+}$ are only of Evans's A-type (Evans, 1964). From fig.4 one can see that O(17)-O(17) and O(13)-O(13) are two pairs of water molecules linked to each other by a double hydrogen bond. This is because from the analysis of O-O distances less than 3.20 Å (Table IV), coupled to the electrostatic requirements (Table VI), only two of the four possible pairs seem available for

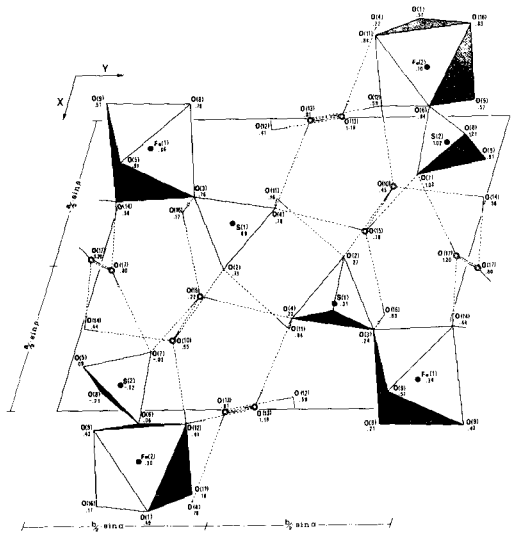


Fig.2. The crystal structure of hohmannite showing the water molecules and the probable hydrogen-bond system. Next to each atom is given its z coordinate.

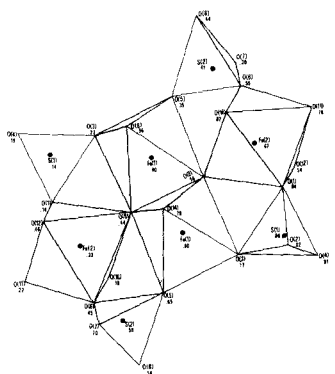

Fig.3. The group of composition $Fe_4(H_2O)_4O_8(SO_4)_4$ found in hohmannite.

Table III. O-S-O and O-Fe-O bond angles with standard deviations in parentheses. The values of hohmannite (this study) are compared with those of amarantite (Süsse, 1966).

| Atoms involved | Angles (this study) | Angles (Süsse) | Atoms involved | Angles (this study) | Angles (Süsse) |
|---|---|---|---|---|---|
| O(3)-Fe(1)-O(5) | 80.6(2)° | 84.9(2)° | O(9)-Fe(2)-O(16)w | 96.1(2)° | 86.3(2)° |
| O(3)-Fe(1)-O(8) | 89.7(2) | 89.8(2) | O(9)-Fe(2)-O(1) | 100.8(2) | 98.9(2) |
| O(3)-Fe(1)-O(9) | 176.7(2) | 169.8(2) | O(11)w-Fe(2)-O(12)w | 84.0(2) | 92.4(2) |
| O(3)-Fe(1)-O(14)w | 83.9(2) | 80.5(2) | O(11)w-Fe(2)-O(16)w | 87.1(2) | 88.5(2) |
| O(3)-Fe(1)-O($\bar{9}$) | 98.2(2) | 95.2(2) | O(11)w-Fe(2)-O(1) | 82.3(2) | 85.9(2) |
| O(5)-Fe(1)-O(8) | 89.5(2) | 82.8(2) | O(12)w-Fe(2)-O(16)w | 171.1(2) | 175.3(2) |
| O(5)-Fe(1)-O(9) | 97.1(2) | 97.5(2) | O(12)w-Fe(2)-O(1) | 93.3(2) | 85.2(2) |
| O(5)-Fe(1)-O(14)w | 86.0(2) | 89.8(2) | O(16)w-Fe(2)-O(1) | 86.4(2) | 93.3(2) |
| O(5)-Fe(1)-O($\bar{9}$) | 178.5(2) | 172.1(2) | | | |
| O(8)-Fe(1)-O(9) | 92.7(2) | 100.3(2) | O(1)-S(1)-O(2) | 109.5(3) | 110.7(3) |
| O(8)-Fe(1)-O(14)w | 172.6(2) | 168.3(2) | O(1)-S(1)-O(3) | 108.3(3) | 107.5(3) |
| O(8)-Fe(1)-O($\bar{9}$) | 91.4(2) | 89.3(2) | O(1)-S(1)-O(4) | 108.9(3) | 109.2(3) |
| O(9)-Fe(1)-O(14)w | 93.6(2) | 89.6(2) | O(2)-S(1)-O(3) | 109.8(3) | 109.2(3) |
| O(9)-Fe(1)-O($\bar{9}$) | 84.0(2) | 83.7(2) | O(2)-S(1)-O(4) | 111.7(3) | 112.7(3) |
| O(14)w-Fe(1)-O($\bar{9}$) | 93.0(2) | 98.0(2) | O(3)-S(1)-O(4) | 108.6(3) | 107.3(3) |
| O(6)-Fe(2)-O(9) | 97.2(2) | 94.4(2) | O(7)-S(2)-O(8) | 108.7(3) | 111.0(3) |
| O(6)-Fe(2)-O(11)w | 80.1(2) | 82.6(2) | O(7)-S(2)-O(5) | 111.0(3) | 110.8(3) |
| O(6)-Fe(2)-O(12)w | 92.5(2) | 84.3(2) | O(7)-S(2)-O(6) | 111.3(3) | 110.1(3) |
| O(6)-Fe(2)-O(16)w | 85.1(2) | 96.5(2) | O(8)-S(2)-O(5) | 108.4(3) | 109.1(3) |
| O(6)-Fe(2)-O(1) | 160.8(2) | 164.0(2) | O(8)-S(2)-O(6) | 108.1(2) | 107.1(3) |
| O(9)-Fe(2)-O(11)w | 175.6(2) | 169.4(2) | O(5)-S(2)-O(6) | 109.3(2) | 108.7(3) |
| O(9)-Fe(2)-O(12)w | 92.7(2) | 91.8(2) | | | |

TABLE IV. Ow - O distances less than 3.20 Å related to oxygen atoms not belonging to the same polyhedron. The asterisk indicates atoms in a different unit cell.

| | | | |
|---|---|---|---|
| O(10)w-O($\bar{2}$) | 2.905(8) Å | O(13)w-O(4) | 2.841(7) Å |
| -O(7) | 3.074(8) | -O(7) | 3.069(7) |
| -O(8) | 3.149(7) | -O($\bar{3}$)w | 2.887(11) |
| -O(1$\bar{2}$)w | 2.725(7) | O(14)w-O*(17)w | 2.687(9) |
| -O($\bar{1}$4)w | 2.711(7) | O(15)w-O*(4) | 2.817(7) |
| -O($\bar{1}$5)w | 2.853(8) | -O*(16)w | 2.647(7) |
| O(11)w-O*(2) | 2.710(7) | -O(7) | 2.834(7) |
| -O(6) | 2.637(6) | O(16)w-O(17)w | 3.070(9) |
| -O($\bar{1}$) | 2.677(7) | -O(1) | 2.762(7) |
| -O($\bar{4}$) | 2.750(6) | -O($\bar{3}$) | 3.052(6) |
| O(12)w -O(6) | 2.904(6) | -O($\bar{5}$) | 2.991(7) |
| -O*(13)w | 2.619(7) | O(17)w-O(7) | 3.003(9) |
| -O(1$\bar{3}$)w | 3.116(7) | -O(17)w | 3.010(14) |
| -O($\bar{1}$) | 2.904(6) | | |

a hydrogen bond: O(17)-O(17) and O(17-O(7). If we suppose that there is also centrosymmetry for the hydrogen bonds, a double hydrogen bond between O(17) and O(17) is the result. From this we derive that O(13) is also stabilized by a double hydrogen bond. The electrostatic valency balance was computed taking into account the individual bond-strength bond-length parameters given by Brown and Shannon (1973). The bond-strengths of O-H...O bonds are derived from the curve of bond valences proposed by Brown and Shannon and further discussed by Donnay and Donnay (1973).

The other two structural water molecules - O(10)w and O(15)w - are surrounded tetrahedrally by four oxygens with bond angles ranging from 84° to 138° and O-O distances from 2.65 to 2.90 Å. According to the system of hydrogen bonds illustrated in fig.2, no hydroxyl groups exist in the structure. In agreement with the chemical composition, the structure suggests eight water molecules, O(10) to O(17), and nine oxygen atoms, O(1) to O(9). In this case the formula $Fe_2(SO_4)_2(OH)_2.7H_2O$ usually quoted for hohmannite seems incorrect, and in the light of the structure determination $Fe_2(H_2O)_4[(SO_4)_2O].4H_2O$ must be preferred.

Relationships between hohmannite and amarantite and conclusions. Hohmannite represents a higher hydrate of amarantite, and has been obtained by a partial dehydration and successive rehydration of amarantite (Cesbron, 1964). The solution of the crystal structure of hohmannite shows the adaptability of the network of amarantite to the admission of two extra water molecules. These minerals are both triclinic with space group $P\bar{1}$; this is because both structures are based on the polymerization of centrosymmetrical groups with composition $Fe_4(H_2O)_4O_8(SO_4)_4$ (fig.3). From a comparison of figs. 2 and 6 one can locate the two new structural water molecules in the network of hohmannite when amarantite hydrates. In fact, in spite of some modifications occurring in the rearrangement of the crystal structure it is still possible to recognize in O(17) the structural water involved in the reaction amarantite + $H_2O$ → hohmannite. The entrance of water into the structure of amarantite has two main effects: the first involves the $Fe_4(H_2O)_4O_8(SO_4)_4$ group and the second the hydrogen-bond system.

The groups just mentioned are forced in hohmannite to adopt changes in configuration, of which the more important is a rotation of the polymerized groups by about 50°. The components of this rotation about 20° and 45° in the crystallographic planes (100) and (001) respectively (compare figs. 1 and 5, also 2 and 6). Of course the reorientation of the groups based on Fe-O-S linkages involves the disruption of the old hydrogen-bond system and the building of a more suitable one (figs. 2 and 6). The crystal structures of amarantite and hohmannite account for the similar dehydration curves found by Scharizer (1927) and by Cesbron (1964). Hohmannite starts dehydrating at a lower temperature than amarantite; the longer O-O distances found for O(17)w and the higher temperature factor for these water molecules (Table 1) agree with this result.

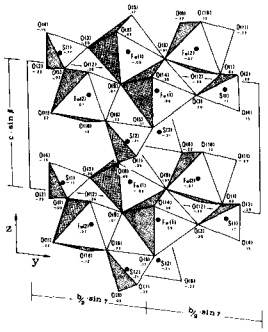

Fig. 5. Chain of octahedra and tetrahedra parallel to the c axis in amarantite. Next to each atom is given its x coordinate.

Table V. Angles involving the ligand water oxygens in agreement with the proton-donors/proton-acceptors scheme proposed in fig.2. The asterisk indicates atoms in a different unit cell.

| | | | |
|---|---|---|---|
| O($\bar{1}$4)w-O(10)w-O(1$\bar{2}$)w | = 97.0(2)° | O($\bar{1}$0)w-O(14)w-O*(17)w | = 100.3(2)° |
| O($\bar{1}$4)w-O(10)w-O($\bar{2}$) | = 124.8(2) | O(7)-O(15)w-O($\bar{1}$0)w | = 96.5(2) |
| O($\bar{1}$4)w-O(10)w-O($\bar{1}$5)w | = 91.1(2) | O(7)-O(15)w-O*(16)w | = 111.7(2) |
| O(1$\bar{2}$)w-O(10)w-O($\bar{2}$) | = 137.8(2) | O(7)-O(15)w-O*(4) | = 111.8(2) |
| O(1$\bar{2}$)w-O(10)w-O($\bar{1}$5)w | = 90.6(2) | O($\bar{1}$0)w-O(15)w-O*(16)w | = 115.9(2) |
| O($\bar{1}$5)w-O(10)w-O($\bar{2}$) | = 83.7(2) | O($\bar{1}$0)w-O(15)w-O*(4) | = 102.0(2) |
| O*(2)-O(11)w-O($\bar{4}$) | = 104.2(2) | O*(4)-O(15)w-O*(16)w | = 116.7(2) |
| O*(13)w-O(12)w-O($\bar{1}$0)w | = 101.8(2) | O*(15)w-O(16)w-O($\bar{3}$) | = 102.3(2) |
| O($\bar{1}$3)w-O(13)w-O(4) | = 106.5(3) | O*(14)w-O(17)w-O($\bar{1}$7)w | = 123.5(4) |
| O*(12)w-O(13)w-O(4) | = 115.3(2) | O($\bar{1}$7)w-O(17)w-O(7) | = 75.5(3) |

Table VI. Electrostatic valency balance in hohmannite.

| Atom | Fe | S | ...H | Sums | Atom | Fe | H-- | ...H | Sums |
|---|---|---|---|---|---|---|---|---|---|
| O(1) | 0.54† | 1.45‡ | - | 1.99 | O(10)w | - | 0.83<br>0.64 | 0.20<br>0.21 | 2.08 |
| O(2) | - | 1.61‡ | 0.16<br>0.21 | 2.04 | | | | | |
| O(3) | 0.46* | 1.44‡ | 0.14 | 2.04 | O(11)w | 0.38† | 0.79<br>0.81 | - | 1.98 |
| O(4) | - | 1.50‡ | 0.19<br>0.18<br>0.18 | 2.05 | O(12)w | 0.47† | 0.80<br>0.76 | - | 2.03 |
| O(5) | 0.46* | 1.465‖ | - | 1.925 | O(13)w | - | 0.82<br>0.83 | 0.24<br>0.17 | 2.06 |
| O(6) | 0.50† | 1.465‖ | - | 1.965 | O(14)w | 0.43* | 0.79<br>0.78 | - | 2.00 |
| O(7) | - | 1.60‖ | 0.18<br>0.15 | 1.93 | O(15)w | - | 0.82<br>0.82 | 0.23<br>0.17 | 2.04 |
| O(8) | 0.46*<br>0.61* | 1.47‖ | - | 1.93 | O(16)w | - | 0.86<br>0.77 | - | 2.04 |
| O(9) | 0.58†<br>0.70† | - | - | 1.89 | O(17)w | - | 0.85<br>0.85 | 0.22<br>0.15 | 2.07 |
| Sums | - | 12.00 | - | - | | 6.00 | 13.02 | 2.98 | 34.00 |

* Fe(1); † Fe(2); ‡ S(1); ‖ S(2). The hydrogen atoms are, or course, members of O(10)w to O(17)w.

Hohmannite loses its structural water below 100°C (as does amarantite). According to Cesbron, in the range 95 to 145°C the TGA curve of hohmannite shows a plateau that corresponds to metahohmannite, $Fe_2(SO_4)_2(OH)_2.3H_2O$. In agreement with this result it seems reasonable to suppose that in hohmannite too there is a group of composition $Fe_4(H_2O)_4O_8(SO_4)_4$. Consequently metahohmannite should represent the lower boundary of the series hohmannite-amarantite-metahohmannite, in which all the structural water is lost.

The crystal structure of hohmannite accounts for the elongation in the [001] direction, for the cleavage (010), (110), and (1$\bar{1}$0) quoted in Dana's System (Palache, Berman, and Frondel, 1951), and for (100) not quoted. It accounts too for the higher refractive indices than those of amatantite.

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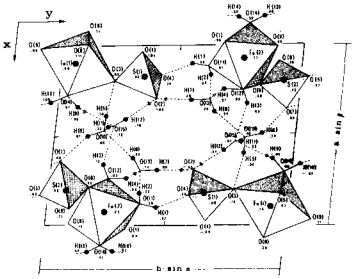

Fig. 6. The crystal structure of amarantite which shows up the water molecules and the related hydrogen-bond system. Next to each atom is given its z coordinate.