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THE CRYSTAL STRUCTURE OF ROEMERITE

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ABSTRACT

The mineral roemerite, $Fe^{2+}Fe_2^{3+}(SO_4)_4 \cdot 14H_2O$, crystallizes in the triclinic space group $P\bar{1}$. The lattice parameters for crystals from Dexter Mine, Utah, are $a = 6.463(8)$ Å, $b = 15.309(18)$ Å, $c = 6.341(8)$ Å, $\alpha = 90°32'(10')$, $\beta = 101°5'(10')$, $\gamma = 85°44'(10')$ with $Z = 1$. A chemical analysis and a thermic study on roemerite from this locality were performed before collecting X-ray single crystal data for the structural study. The crystal structure was solved by a three-dimensional Patterson synthesis employing a total of 3532 reflections collected by the precession apparatus. The R value on 2320 observed reflections is 0.061.

The structure consists of isolated $[Fe(H_2O)_6]^{2+}$ and $[Fe(H_2O)_4(OSO_3)_2]^{1-}$ groups. These groups are weakly connected to each other by a system of hydrogen bonds. The Fe ions are surrounded octahedrally by oxygen atoms. The ferrous iron coordinates with six water molecules at an average distance of 2.112 Å. The ferric iron binds four water molecules and two oxygen atoms belonging to different SO_4 groups in *cis*-configuration with mean distances of 2.033 and 1.939 Å respectively. The sulfate groups show the normal tetrahedral form with a mean S-O value of 1.474 Å.

INTRODUCTION

The structural investigation of some iron sulfates was undertaken in our laboratory in order to obtain a better crystallochemical knowledge of this widespread class of minerals. The present paper, concerning the structural determination of roemerite, is a first result of our research; the crystal structures of copiapite and butlerite are at present under investigation.

Roemerite, a hydrated sulfate of ferrous and ferric iron with chemical formula $Fe^{2+}Fe_2^{3+}(SO_4)_4 \cdot 14H_2O$, was found at Rammelsberg (Germany) by Grailich (1858). The morphology of the crystals was first studied by Blaas (1884) who assigned the mineral to the triclinic system. Different axial settings were used by successive investigators, until Wolfe (1937) proposed a reorientation of roemerite according to a more acceptable triclinic setting. Wolfe's normal setting corresponds to the structural cell determined from X-ray data by Van Loan and Nuffield (1959). From morphological considerations, on crystals from Island Mountain, California, these authors assigned roemerite to the space group $P\bar{1}$.

From a genetic point of view, roemerite is generally the result of an oxidation of iron sulfides. Conditions for the formation of roemerite and associated sulfates have been discussed by Bandy (1938) for the deposits of Alcaparrosa and Quetena (Northern Chile). In these localities the mineral seems to be formed in the early phase of pyrite oxidation and shows alteration to coquimbite and other ferric normal or basic sulfates.

Our specimen, coming from Dexter Mine, Utah, consists of clusters and bunches exhibiting scattered tiny crystals showing cuboidal habitus, brownish honey colour and vitreous to resinous luster. In the sample, roemerite is associated with alunite, halotrichite and quartz.

CHEMICAL DATA

Chemical analyses have been published for roemerite from different localities: the presence of Zn, Na, Mg, Ca, and Al may occur to various extents in the mineral, as well as variations in the water content. Since chemical data for roemerite from Dexter Mine are lacking, it was necessary to carry out an analysis on crystals from this source before undertaking the structural study. The results are reported in Table 1 with those of other authors.

The analysis on the material selected as pure as it was possible confirms the atomic ratio $Fe^{2+}/Fe^{3+}=1/2$. The H_2O content is lower than the value calculated assuming as correct the chemical formula derived from the X-ray investigation. This can be explained only by a larger weathering of roemerite from Dexter Mine in respect of the same materials from other localities, and suggests the presence of less hydrated sulfates as alteration products. Microanalytical qualitative tests do not reveal the presence of Zn, Na, Mg, Ca, and Al. The water content of the

TABLE 1. CHEMICAL ANALYSES OF ROEMERITE, WEIGHT PERCENT

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
FeO	6.26	5.80	8.71	6.94	7.01	8.78	9.73	8.94
ZnO	1.97	3.06						
MgO		0.25				0.14		
CaO	0.58					0.62		
Na_2O					0.88			
Fe_2O_3	20.63	19.77	20.11	20.60	20.84	19.55	21.39	19.86
Al_2O_3					2.55	1.45		
SO_3	41.54	39.71	39.79	38.30	39.34	38.40	40.02	39.83
H_2O	28.00	31.17	30.99	33.40	31.33	30.98	28.71	31.37
Total	98.98	99.76	99.60	99.24	101.95	99.92	99.85	100.00

(1) From Rammelsberg, Harz (Tschermak, in Grailich, 1858).
(2) From Rammelsberg, Harz (Scharizer, 1903).
(3) From Tierra Amarilla, Chile (Scharizer, 1903).
(4) From Island Mountain, California (Landon, 1927).
(5) From United Verde Mine, Jerome, Arizona (Buehrer in Lausen, 1928).
(6) From Pfaffenreuth, Bavaria (Gossner and Drexler, 1935).
(7) From Dexter Mine, Utah (present work).
(8) Theoretical analysis assuming the ideal formula $Fe^{2+}Fe_2^{3+}(SO_4)_4\cdot 14H_2O$ for roemerite.

mineral was determinated from a thermogravimetric analysis made on a 100 mg sample.

THERMAL DATA

Thermogravimetric, differential thermogravimetric and differential thermal curves are shown in Figure 1. From the thermogravimetric curve the mineral appears to gradually lose water. At 180°C it has lost 22.16 weight percent; this weight is equivalent to 77.18 percent of the total water content in roemerite. Further heating is accompanied by a weight loss step by step, until, at 315°C, the material has lost 28.71 weight percent. At this stage the water loss seems to be completed. The behaviour of Dexter Mine roemerite on heating is in agreement with that determined by Scharizer (1903) on material from Rammelsberg and South America. The differential thermal analysis curve exhibits a first endothermic peak with maximum at 155°C which coalesces with a second endothermic peak at 175°C. Two other well-defined peaks are present at 215°C and 310°C respectively. This curve agrees with that reported by Cocco (1952) for Rammelsberg roemerite.

SINGLE-CRYSTAL X-RAY STUDY

Experimental. A suitable crystal with a rounded shape was oriented on the precession camera with the b^* axis as the spindle axis. With this crystal mounting five reciprocal-cell parameters were obtained from film measurements on $0kl$ and $hk0$ photographs; the direct-cell β angle was measured from two accurate dial settings. For the cell dimensions the following values were obtained:

$a = 6.463 \pm 0.008$ Å $\quad \alpha = 90°32' \pm 10'$
$b = 15.309 \quad 0.018 \quad \beta = 101°5' \quad 10'$
$c = 6.341 \quad 0.008 \quad \gamma = 85°44' \quad 10'$

These constants are in agreement with those of Van Loan and Nuffield. The density, calculated for one formula unit per cell, is 2.173 g/cm^3, in agreement with the mean measured value 2.18 g/cm^3.

Diffraction effects from reciprocal lattice planes $0kl$-$3kl$ and $hk0$-$hk3$ were recorded on films by an integrating precession apparatus using Mo $K\alpha$ radiation. The intensity data were measured with a microdensitometer. Lorentz-polarization correction was made using a program written by Catani and Zanazzi (1965) for the IBM 1620 computer. An approximate absorption correction was applied to the data assuming the crystal to be exactly spherical in shape, with $\mu R = 0.8$.

The values for F^2 were placed on a single scale by correlating the common reflections occurring on the films. 3532 independent diffraction effects were collected, 1212 of which were not observed. To these reflections an F value just below the observational limit was assigned and their contribution was excluded from calculations.

Structure determination and refinement. According to the chemical formula the ferrous iron must occupy a special position and therefore it was located on the inversion center at the origin of the cell. The locations of ferric iron and the two sulfur atoms in the asymmetric unit were obtained from a three-dimensional Patterson function. The positions of all oxygen atoms were easily detected by a Fourier synthesis computed with the signs given

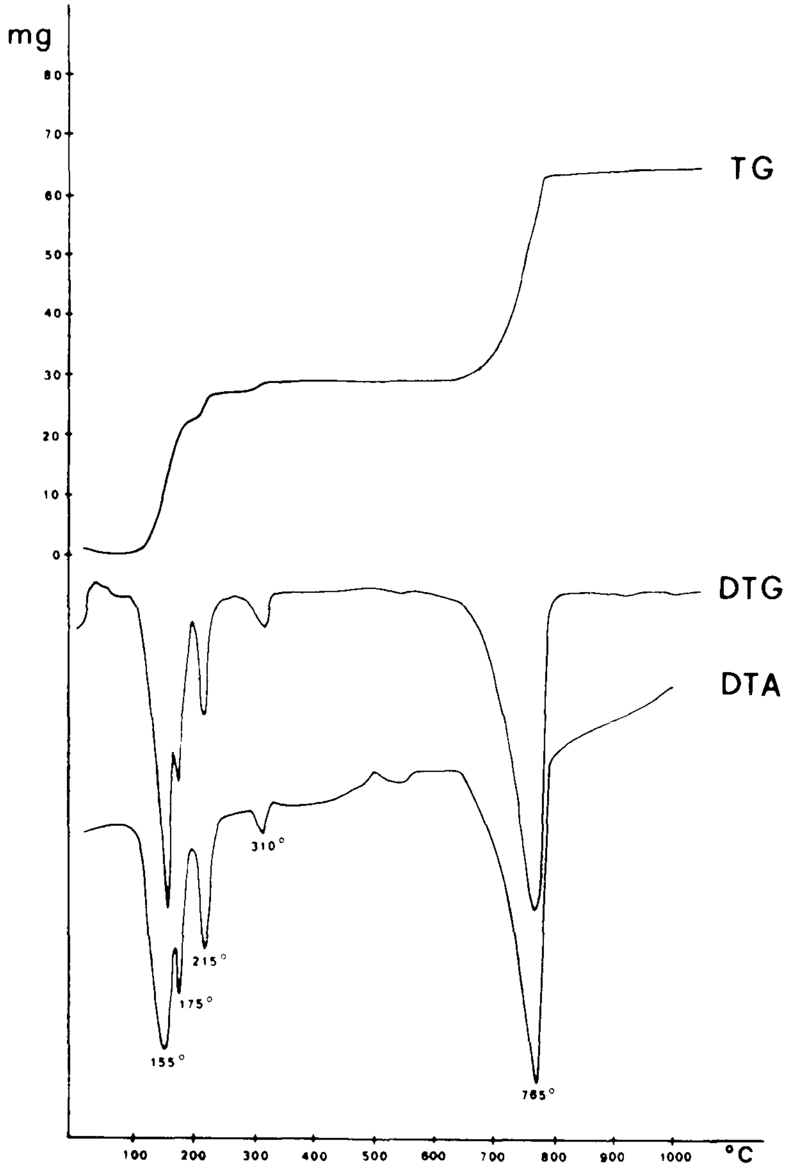

FIG. 1. Thermogravimetric (TG), differential thermogravimetric (DTG) and differential thermal (DTA) curves of roemerite. Rate of heating: 10°C/min.; thermocouple Pt/ Pt + 10% Rh; reference material Al_2O_3.

to the structure factors by the heavier atoms. A first improvement of the structure was carried out by successive electron density maps to a reliability index $R = \Sigma\,||F_o| - |F_c||/\Sigma|F_o|$ of 0.19.

The further refinement of the structure was carried out by means of the least squares method. Reflections were given weights according to the following scheme: $\sqrt{w} = 1$ for reflexions with $F_o \leq 4\,F_{\min}$; $\sqrt{w} = 4\,F_{\min}/F_o$ for $F_o > 4\,F_{\min}$. In the first stages a block diagonal program written by Albano, Pompa, Bellon e Scatturin (1963) for the IBM 1620 computer was employed; positional parameters and individual isotropic temperature coefficients were varied. After four cycles, when the R index was 0.10, the refinement was continued by the full-matrix program of Busing and Levy, adapted for the IBM 7090 computer by J. M. Stewart of the University of Maryland (1964)[1]. Individual anisotropic temperature factors were applied and the R index dropped to 0.069 in three cycles.

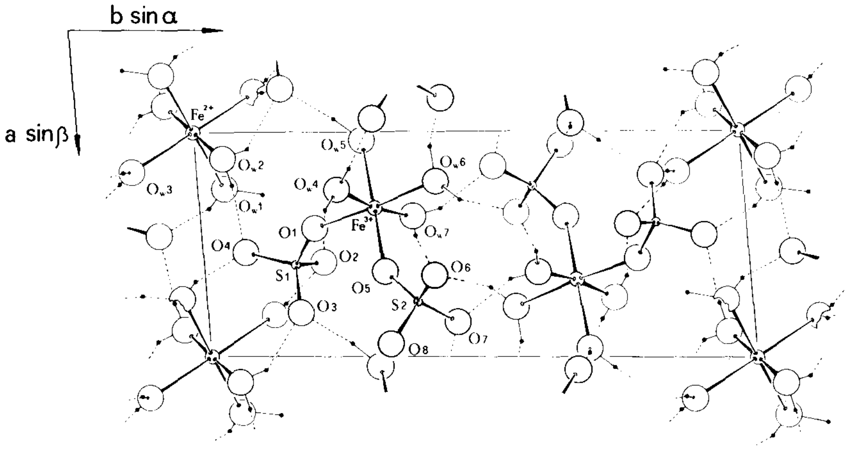

FIG. 2. The crystal structure of roemerite viewed along [001].

At this stage a difference Fourier synthesis was computed. On the maps, small peaks were found at, or very closely to, the positions expected for hydrogen atoms. With the contribution of these atoms, to which an overall isotropic thermal parameter of 5 Å^2 was assigned, a last cycle of refinement was carried out. Since the number of parameters exceeded the 180-variables capacity of the full-matrix least-squares program, it was necessary to refine with the block-diagonal approximation. In this cycle thermal parameters of hydrogen atoms were left fixed. The final R index is 0.061 for all observed reflections.

Observed and calculated structure factors are listed in Table 2.[2] The atomic scattering factors given by Cromer and Waber (1965) for Fe^{2+}, Fe^{3+}, S, O and H were used.

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[1] Calculations were performed with the IBM 7090 computer of the Centro Nazionale Universitario di Calcolo Elettronico of the Pisa University.

[2] To obtain a copy of Table 2, listing observed and calculated structure factors of roemerite, order NAPS Document #00710 from ASIS National Auxiliary Publications Service, c/o CCM Information Sciences, Inc., 22 West 34th Street, New York, New York 10001; remitting $1.00 for microfiche or $3.00 for photocopies, in advance payable to ASIS-NAPS.

DISCUSSION OF THE STRUCTURE

The structure of roemerite projected along the *c* axis is shown in Figure 2. Table 3 gives the atomic coordinates and Table 4 shows the anisotropic thermal parameters and the isotropic equivalents calculated according to Hamilton (1959). Interatomic distances and angles are listed in Tables 5 and 6.

The Fe ions are surrounded octahedrally by oxygen atoms; the sulfate groups have the normal tetrahedral form.

The ferrous iron at the origin of the cell coordinates six water molecules

TABLE 3. FRACTIONAL ATOMIC COORDINATES WITH THEIR STANDARD DEVIATIONS IN PARENTHESES

Atom	*x*	*y*	*z*
Fe^{2+}	0.00000	0.00000	0.00000
Fe^{3+}	.33850 (11)	.32040 (5)	.59415 (12)
S (1)	.59285 (20)	.16794 (8)	.36415 (21)
S (2)	.75980 (18)	.38682 (8)	.90730 (21)
O (1)	.43090 (68)	.20817 (27)	.48397 (73)
O (2)	.58301 (76)	.21947 (32)	.16464 (73)
O (3)	.80677 (60)	.16991 (27)	.49380 (70)
O (4)	.53956 (72)	.07819 (30)	.32383 (91)
O (5)	.62142 (65)	.33029 (29)	.75584 (75)
O (6)	.64356 (68)	.42242 (27)	1.06814 (72)
O (7)	.82510 (67)	.45660 (27)	.78307 (78)
O (8)	.94487 (60)	.33021 (27)	1.00778 (65)
O_w (1)	.25089 (89)	.04938 (49)	−.12957 (102)
O_w (2)	.11209 (77)	.04923 (35)	.31091 (81)
O_w (3)	.17529 (102)	−.11732 (35)	.09135 (79)
O_w (4)	.25760 (62)	.25577 (27)	.84407 (64)
O_w (5)	.03495 (59)	.30719 (26)	.44316 (63)
O_w (6)	.21791 (65)	.43565 (26)	.69570 (73)
O_w (7)	.37811 (65)	.38822 (26)	.33431 (69)
H (1)	.337 (18)	.018 (7)	−.175 (19)
H (2)	.276 (19)	.117 (7)	−.134 (19)
H (3)	.233 (19)	.063 (7)	.350 (19)
H (4)	.065 (19)	.095 (8)	.358 (20)
H (5)	.170 (19)	−.141 (7)	.205 (20)
H (6)	.225 (19)	−.147 (8)	.014 (20)
H (7)	.343 (19)	.231 (7)	.935 (19)
H (8)	.160 (19)	.277 (7)	.908 (20)
H (9)	−.040 (19)	.259 (7)	.440 (20)
H (10)	.011 (19)	.302 (7)	.311 (19)
H (11)	.300 (19)	.477 (7)	.789 (19)
H (12)	.055 (19)	.431 (8)	.709 (20)
H (13)	.337 (18)	.440 (7)	.315 (20)
H (14)	.460 (19)	.389 (8)	.237 (20)

TABLE 4. ANISOTROPIC THERMAL PARAMETERS WITH THEIR STANDARD DEVIATIONS AND EQUIVALENT ISOTROPIC TEMPERATURE FACTORS AFTER HAMILTON FOR NON-HYDROGEN ATOMS[a]

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	$\overline{B}$(Å^2)
Fe^{2+}	0.01149 (25)	0.00228 (5)	0.01122 (28)	0.00039 (8)	0.00195 (26)	−0.00044 (9)	1.92
Fe^{3+}	.00569 (13)	.00159 (2)	.00739 (15)	− .00029 (4)	.00109 (14)	− .00032 (5)	1.18
S (1)	.00801 (24)	.00195 (5)	.00938 (28)	.00002 (8)	.00156 (27)	− .00049 (9)	1.53
S (2)	.00610 (22)	.00175 (4)	.00894 (27)	− .00013 (7)	.00117 (25)	− .00034 (8)	1.34
O (1)	.01449 (94)	.00258 (17)	.01816 (115)	.00020 (31)	.00669 (102)	− .00159 (35)	2.45
O (2)	.01747 (117)	.00433 (23)	.01460 (113)	.00125 (41)	.00317 (110)	.00305 (41)	3.06
O (3)	.00897 (81)	.00316 (18)	.01684 (112)	− .00031 (30)	− .00026 (92)	.00187 (35)	2.38
O (4)	.01480 (104)	.00303 (19)	.03153 (165)	− .00123 (35)	.00593 (122)	− .00421 (45)	3.32
O (5)	.01099 (89)	.00353 (19)	.01896 (122)	− .00055 (33)	− .00141 (99)	− .00182 (38)	2.75
O (6)	.01530 (99)	.00260 (16)	.01795 (114)	.00006 (32)	.00741 (104)	− .00103 (34)	2.47
O (7)	.01440 (99)	.00272 (17)	.02191 (126)	.00017 (32)	.00738 (108)	.00206 (37)	2.67
O (8)	.00972 (83)	.00329 (18)	.01240 (98)	.00084 (30)	.00177 (88)	.00094 (33)	2.21
O_w (1)	.02611 (146)	.00352 (23)	.03803 (193)	− .00260 (47)	.01871 (160)	− .00484 (54)	4.16
O_w (2)	.01533 (113)	.00507 (26)	.02070 (131)	− .00038 (43)	.00127 (117)	− .00401 (47)	3.52
O_w (3)	.04033 (191)	.00439 (24)	.01428 (119)	.00749 (55)	.00947 (139)	.00179 (43)	4.33
O_w (4)	.01071 (88)	.00335 (18)	.01089 (95)	− .00005 (31)	.00220 (89)	.00055 (32)	2.18
O_w (5)	.00954 (80)	.00318 (17)	.01019 (90)	− .00122 (29)	.00009 (84)	− .00020 (31)	2.05
O_w (6)	.01343 (94)	.00230 (16)	.02071 (120)	− .00061 (30)	.00652 (101)	.00247 (34)	2.42
O_w (7)	.01445 (97)	.00248 (16)	.01668 (107)	.00055 (31)	.00850 (100)	.00157 (34)	2.30

[a] The anisotropic thermal factors are in the form: $T=\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$

at an average distance of 2.112 Å, the individual distances lying between 2.076 and 2.141 Å. These distances are in good agreement with those found in melanterite (Baur, 1964), a structure containing isolated $[Fe(H_2O)_6]^{2+}$ octahedra. In this mineral, the mean value for the Fe-O bond length is 2.124 Å, with distances in the range 2.068–2.188 Å.

The ferric iron links four water molecules and two oxygen atoms belonging to different SO_4 groups. The resulting $[Fe(H_2O)_4(OSO_3)_2]^{1-}$ group has a *cis*-configuration of ligands in the octahedron. The distances between ferric ion and water molecules are in the range 2.023–2.047 Å (mean value: 2.033 Å); the two oxygen atoms are bonded with shorter distances: 1.945 and 1.933 Å. Reliable information on Fe^{3+}—O distances in isolated octahedra is scarce. The values found here are slightly lower than those found in metastrengite (Fanfani and Zanazzi, 1966), a phosphate mineral where ferric iron octahedrally coordinates two water molecules at an average distance of 2.060 Å, and four oxygen atoms of different PO_4 groups with bond lengths in the range 1.956–1.988 Å (mean value: 1.973 Å). In krausite (Graeber, Morosin and Rosenzweig, 1965) the iron atom is coordinated to five sulfate-oxygen atoms with an average bond length of 1.989 Å and to one water molecule completing the octahedral configuration, at a distance of 2.029 Å.

TABLE 5. BOND LENGTHS WITH THEIR STANDARD DEVIATIONS IN PARENTHESES

Fe^{2+}—O_w (1)	2.141 (7) Å (×2)	S (1)—O (1)	1.501 (5) Å
—O_w (2)	2.118 (6) (×2)	—O (2)	1.496 (5)
—O_w (3)	2.076 (7) (×2)	—O (3)	1.469 (5)
		—O (4)	1.450 (5)
Fe^{3+}—O (1)	1.945 (5) Å		
—O (5)	1.933 (5)	S (2)—O (5)	1.497 (5) Å
—O_w (4)	2.047 (5)	—O (6)	1.458 (5)
—O_w (5)	2.035 (5)	—O (7)	1.466 (5)
—O_w (6)	2.025 (5)	—O (8)	1.467 (5)
—O_w (7)	2.023 (5)		

The two SO_4 coordination polyhedra show the usual tetrahedral shape with a mean S-O value of 1.476 Å and 1.472 Å in good agreement with the values found in melanterite, 1.474 Å (Baur, 1964), in amarantite, 1.476 and 1.478 Å (Süsse, 1968), and in krausite, 1.467 and 1.474 Å (Graeber, Morosin and Rosenzweig, 1965).

An interesting feature consists in a significant lengthening of S-O distances when the oxygen atom is linked to an iron ion. In the present structure, both SO_4 tetrahedra share one vertex with the ferric iron coordination octahedron. The S-O distances involving the oxygen atom

TABLE 6. BOND ANGLES WITH THEIR STANDARD DEVIATIONS IN PARENTHESES

O_w (1)—Fe^{2+}—O_w (2)	93.2 (3)°	O (1)—S (1)—O (2)	108.7 (3)°
—O_w (2)′	86.8	—O (3)	110.8
—O_w (3)	92.2	—O (4)	105.4
—O_w (3)′	87.8	O (2)—S (1)—O (3)	108.2
O_w (2)—Fe^{2+}—O_w (3)	88.8	—O (4)	113.3
—O_w (3)′	91.2	O (3)—S (1)—O (4)	110.2
O (1)—Fe^{3+}—O (5)	89.5 (2)°	O (5)—S (2)—O (6)	109.2 (3)°
—O_w (4)	89.0	—O (7)	108.5
—O_w (5)	91.2	—O (8)	106.5
—O_w (6)	175.3	O (6)—S (2)—O (7)	111.5
—O_w (7)	93.8	—O (8)	110.9
O (5)—Fe^{3+}—O_w (4)	91.0	O (7)—S (2)—O (8)	110.1
—O_w (5)	176.0		
—O_w (6)	95.2		
—O_w (7)	95.8		
O_w (4)—Fe^{3+}—O_w (5)	85.1		
—O_w (6)	90.6		
—O_w (7)	172.6		
O_w (5)—Fe^{3+}—O_w (6)	84.1		
—O_w (7)	88.0		
O_w (6)—Fe^{3+}—O_w (7)	86.0		

coordinated to iron are 1.501 and 1.497 Å, respectively for S(1) and S(2) tetrahedra and are significantly longer than the mean values of the three oxygen atoms not bonded to the cation (1.468 and 1.464 Å).

Something analogous happens in the crystal structures of krausite and amarantite. In the first structure each of the two SO_4 groups shares an edge with an iron octahedron. The average bond lengths for oxygen atoms linked to iron are 1.497 and 1.494 Å, which may be compared with 1.451 and 1.463 Å for oxygen atoms not bonded to the iron ion. In amarantite one SO_4 tetrahedron shares three corners with three different Fe-octahedra, while the second one shares only two. In the first case the mean value S-O_{Fe} is 1.491 Å against a bond length S-O 1.439 Å, in the second case the mean value for S-O_{Fe} is 1.496 Å against an average S-O bond of 1.456 Å.

The lengthening of S-O distance for oxygen atoms linked to the iron ion can be related to a lower coordinative π-effect caused by a decrease of effective negative charge on oxygen atoms coordinated by the cations.

The roemerite structure consists of isolated $[Fe(H_2O)_6]^{2+}$ octahedra located at the eight vertices of the unit cell and of two $[Fe(H_2O)_4(OSO_3)_2]^{1-}$ groups, each formed by the coordination octahedron around

Fe^{3+} and by the two SO_4 tetrahedra, placed in the cell around the inversion center at 1/2, 1/2, 1/2.

These components of the structure are linked together by hydrogen bonds. The H-bond distances and angles are listed in Table 7. It is interesting to note that, in roemerite, only the oxygen atoms belonging

TABLE 7. HYDROGEN-BOND DISTANCES AND ANGLES

(I) $-1+x, y, z$
(II) $x, y, 1+z$
(III) $-1+x, y, -1+z$
(IV) $x, y, -1+z$
(V) $1-x, -y, -z$
(VI) $1-x, -y, 1-z$
(VII) $1-x, 1-y, 2-z$
(VIII) $1-x, 1-y, 1-z$

Atoms			Angles	Distances (Å)		
A	B	C	ABC	AB	AC	BC
O (4) (V)	···· H (1)	—O_w (1)	161°	1.95	2.71	0.80
	H (2)	—O_w (1)	—	—	—	1.06
H (1)	— O_w (1)	—H (2)	114°			
O (4)	···· H (3)	—O_w (2)	156°	2.05	2.82	0.82
O (3) (I)	···· H (4)	—O_w (2)	149°	2.26	2.99	0.82
H (3)	— O_w (2)	—H (4)	91°			
O (3) (VI)	···· H (5)	—O_w (3)	165°	1.94	2.74	0.82
O (2) (V)	···· H (6)	—O_w (3)	169°	2.09	2.84	0.76
H (5)	— O_w (3)	—H (6)	114°			
O (2) (II)	···· H (7)	—O_w (4)	156°	1.91	2.66	0.79
O (8) (I)	···· H (8)	—O_w (4)	172°	1.78	2.63	0.86
H (7)	— O_w (4)	—H (8)	105°			
O (3) (I)	···· H (9)	—O_w (5)	168°	1.82	2.64	0.84
O (8) (III)	···· H (10)	—O_w (5)	167°	1.93	2.74	0.82
H (9)	— O_w (5)	—H (10)	89°			
O (6) (VII)	···· H (11)	—O_w (6)	158°	1.80	2.73	0.98
O (7) (I)	···· H (12)	—O_w (6)	159°	1.66	2.70	1.08
H (11)	— O_w (6)	—H (12)	118°			
O (7) (VIII)	···· H (13)	—O_w (7)	163°	1.87	2.67	0.82
O (6) (IV)	···· H (14)	—O_w (7)	163°	1.85	2.71	0.89
H (13)	— O_w (7)	—H (14)	93°			

The estimated standard deviations are 0.12 Å for the distances O—H and O · · · H, less than 0.01 Å for the distances O_w · · · O, 10° for the angles O · · · H—O_w and H—O_w—H.

TABLE 8. BALANCE OF ELECTROSTATIC VALENCES FOR OXYGEN ATOMS

	Fe^{3+}	Fe^{2+}	S	−H · · ·	· · · H−	−H	Total
O (1)	1/2		3/2				2
O (2)			3/2		2×1/4		2
O (3)			3/2		2×1/4		2
O (4)			3/2		2×1/4		2
O (5)	1/2		3/2				2
O (6)			3/2		2×1/4		2
O (7)			3/2		2×1/4		2
O (8)			3/2		2×1/4		2
O_w (1)		1/3		3/4		1	2+1/12
O_w (2)		1/3		3/4		1	2+1/12
O_w (3)		1/3		2×3/4			2−2/12
O_w (4)	1/2			2×3/4			2
O_w (5)	1/2			2×3/4			2
O_w (6)	1/2			2×3/4			2
O_w (7)	1/2			2×3/4			2

to the sulfate groups and not coordinated to the ferric ion, exhibit the function of proton acceptors in the system of hydrogen bonds. In fact each pair of hydrogen atoms of the water molecules forms hydrogen bridges with these oxygen atoms with the exception of H(2) which does not seem to be involved in the hydrogen-bond system. In roemerite the hydrogen bonds show a close range of distances (2.62–2.84 Å), if we neglect one larger distance $O_w(2)$–O(3) (2.99 Å). However, the location of hydrogen atoms proves the presence of a weak interaction also in this case.

Assuming the structure as entirely ionic, a scheme of the electrostatic valences for oxygen atoms was derived. The cation contribution was considered as the ratio between the valence and the coordination number. Each hydrogen contribution was distributed among two oxygen atoms as +3/4 for the linked one and +1/4 for the unlinked atom. The results are listed in Table 8.

The crystal structure accounts for some physical properties of roemerite: the existence of isolated groups of coordination polyhedra can explain the cuboidal habitus of the crystals. The perfect {010} cleavage may be explained by considering the weakness of the linkages in this plane where only relatively weak hydrogen bonds occur through the two $[Fe(H_2O)_4(OSO_3)_2]^{1-}$ groups in the cell.

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