The crystal structure of the monoclinic $Fe_2(SO_4)_3$

By P. C. CHRISTIDIS and P. J. RENTZEPERIS

Applied Physics Laboratory, Aristotle University of Thessaloniki

Auszug

Die Kristallstruktur des monoklinen $Fe_2(SO_4)_3$ wurde mit Hilfe dreidimensionaler Diffraktometer-Daten (Philips PW 1100) bestimmt. Die Struktur wurde aus der dreidimensionalen Patterson-Synthese mit Hilfe der Minimum-Funktion ermittelt. Die Gitterkonstanten, ermittelt nach der Methode der kleinsten Quadrate mit direkt auf dem Diffraktometer gemessenen θ-Werten, sind: $a = 8,2955$, $b = 8,5332$, $c = 11,6304$ Å, $\beta = 90,25°$; $Z = 4$, Raumgruppe $P2_1/n$. Atomparameter und anisotrope Temperaturfaktoren wurden nach der Methode der kleinsten Quadrate bis zu $R = 0,038$ verfeinert. Korrekturen für anomale Dispersion und sekundäre Extinktion wurden berücksichtigt.

In der asymmetrischen Einheit der Elementarzelle befinden sich drei verschiedene, fast regelmäßige SO_4-Tetraeder. Die Mittelwerte der (S—O)-Abstände sind in den drei Tetraedern praktisch gleich: 1,468, 1,466, 1,466 Å. Die entsprechenden mittleren (O—O)-Abstände sind 2,397, 2,394 und 2,394 Å; die tetraedrischen Valenzwinkel weichen vom Idealwert 109,46° weniger als um 2,5° ab. Die zwei Fe-Atome in der asymmetrischen Einheit sind oktaedrisch koordiniert. Beide FeO_6-Oktaeder sind nur wenig verzerrt. Die mittleren (Fe—O)-Abstände in den zwei Oktaedern sind 1,980 Å bzw. 1,994 Å, die entsprechenden mittleren (O—O)-Abstände 2,800 Å bzw. 2,822 Å.

Alle Koordinationspolyeder sind isoliert. Die SO_4-Tetraeder haben ihre Spitzen mit je einem FeO_6-Oktaeder gemeinsam und bilden auf diese Weise ein dreidimensionales Gerüst von Tetraedern und Oktaedern, in welchem jedes O-Atom mit nur je einem S- und einem Fe-Atom verbunden ist.

Abstract

The crystal structure of the monoclinic $Fe_2(SO_4)_3$ has been determined using three-dimensional intensities, measured with an automated Philips PW 1100 single-crystal diffractometer. The structure was essentially obtained from the three-dimensional Patterson synthesis by applying the minimum function. The cell constants, obtained by least-squares from direct θ-value measurements on the diffractometer, are: $a = 8.2955$, $b = 8.5332$, $c = 11.6304$ Å, $\beta = 90.25°$; $Z = 4$; the space group is $P2_1/n$. Atomic parameters and anisotropic temper-

ature factors were refined by least-squares to $R = 0.038$. Corrections for anomalous dispersion and secondary extinction were applied.

There are three different and almost regular SO_4 tetrahedra in the asymmetric unit of the cell. The S—O distances are virtually equal, their average values in the three tetrahedra being 1.468, 1.466 and 1.466 Å respectively. The corresponding average O—O distances are 2.397, 2.394 and 2.394 Å and the tetrahedral bond angles deviate from the ideal value 109.46° by less than 2.5°. The two Fe atoms in the asymmetric unit are octahedrally coordinated. Both of the FeO_6 octahedra are only slightly distorted. The average Fe—O distances in the two octahedra are 1.980 Å and 1.994 Å respectively, whereas the corresponding average O—O distances are 2.800 Å and 2.822 Å.

All the coordination polyhedra are isolated. The SO_4 tetrahedra share each of their vertices with a FeO_6 octahedron, thus forming a three-dimensional network of tetrahedra and octahedra, in which each O atom is bonded to only one S and one Fe atom.

Introduction

Anhydrous ferric sulfate, $Fe_2(SO_4)_3$, is known to exist in two modifications, one rhombohedral and one monoclinic (KOKKOROS, 1965). Both yield well-formed transparent, light-pink crystals. The crystals of the rhombohedral modification are almost isometric, cube-like rhombohedra in combination with triangular pinacoidal planes (0001). The monoclinic crystals are tabular or prismatic.

Cell constants and space groups of both modifications were determined by KOKKOROS, who kindly set all the material of his investigation at our disposal. The structure determination of both modifications was undertaken within the framework of a larger program comprising the systematic investigation of the anhydrous sulfates of various trivalent metals. The structure of the rhombohedral modification of $Fe_2(SO_4)_3$ will appear shortly (CHRISTIDIS and RENTZEPERIS, 1975).

Experimental

For the preparation of the anhydrous ferric sulfate a number of methods have been proposed, a detailed description of which is given in GMELIN (1930) and in MELLOR (1953). In our case, well-formed single crystals of both $Fe_2(SO_4)_3$ modifications were obtained by the method described by KOKKOROS (1965): To a heated aqueous solution of $FeSO_4 \cdot 7H_2O$, surplus sulfuric acid was added and the solution was left to evaporate very slowly over a sandbath. Crystals of only one modification, usually the monoclinic, or of both modifications together were obtained, depending on the concentration of the solution, the quantity of the sulfuric acid added, and the temperature at

which evaporation took place. The crystals are relatively stable, especially after tempering at 200 °C until all traces of adsorbed sulfuric acid are driven off. In the air they absorb moisture rather slowly, transforming into a hydrated salt.

A well-developed, transparent monoclinic single crystal was selected, placed into a special Nonius sphere grinder and shaped into a small sphere, 0.3 mm in diameter. To avoid the influence of moisture during shaping, a dry nitrogen stream was used. The sphere was put in a Lindemann capillary tube and centered on a computer-controlled Philips PW 1100 four-circle, single-crystal diffractometer. The cell constants were determined first by using the peak-hunting routine and then the lattice-constants routine of the instrument. To obtain greater accuracy, the θ angles of 80 strong reflections with large θ values were directly measured on the diffractometer and subsequently used in the least-squares program PARAM (part of the *X-ray System of crystallographic programs*; see STEWART *et al.*, 1972). The final values obtained are given in Table 1, together with those of KOKKOROS (1965) for comparison. From systematic absences the space group was confirmed to be C_{2h}^5—$P2_1/n$.

Table 1. *Unit-cell data for monoclinic* Fe₂(SO₄)₃
(Standard errors, given in parentheses, refer to the last digit)

	This investigation	KOKKOROS (1965)
a	8.2955 (12) Å	8.296 Å
b	8.5332 (9)	8.515
c	11.630 (2)	11.60
β	90.75 ° (1)	90.50 °
V	823.21 Å³	819.42 Å³
Z	4	4

ϱ_{meas} = 3.20 g · cm⁻³ (KOKKOROS, 1965).
ϱ_{calc} = 3.225 g · cm⁻³.
Space group: $P2_1/n$.

Three-dimensional intensity data were collected on the PW 1100 diffractometer in the ω-scan mode, using MoKα radiation, monochromated with a graphite monochromator. The intensities of 4457 independent reflections (having maximum $h = 11$, $k = 12$, and $l = 15$) in the asymmetric unit of the reciprocal lattice were measured. Of these 1043 had intensities lower than the background and were treated as weak, by applying to them the HAMILTON (1955) correction.

Integrated intensities were converted to $|F_o|$ values in the usual way. Spherical absorption correction for $\mu = 43.77$ cm^{-1} was applied. For all subsequent computations, the programs of the *X-ray System of crystallographic programs* (Stewart et al., 1972) were used throughout.

Determination of the structure and refinement

The structure was essentially solved from the three-dimensional Patterson synthesis by applying the minimum function, but the position of some O atoms was found from difference Fourier maps. On the Harker line appeared five maxima which could be considered as potential reflection satellites and the corresponding Patterson sections were compared with the Harker section at $y = \frac{1}{2}$ in the usual way. The position of the two Fe atoms and the three S atoms in the asymmetric unit of the cell was immediately clear on the first M_2 map, correponding to the one Fe atom. The M_2 function of the second Fe atom was drawn and then combined with the first M_2 to give an M_4 function. Besides the cations, the position of some O atoms was revealed. A difference Fourier synthesis at this stage yielded all the the O atoms. Structure factor calculation gave $R = 0.346$.

Refinement of the structure was carried out by least squares, using the program CRYLSQ of the *X-ray System*. The fully ionized state was assumed for all the atoms and probable isotropic temperature factors were assigned to them. Atomic-form factors, and anomalous dispersion correction for Fe^{3+}, were obtained from the *International tables* (1968). Scattering factors for S^{6+} and O^{2-} were taken from James and Brindley (1931). A single scale factor was used for the whole set of reflection data.

With isotropic temperature factors and unit weights, refinement resulted in $R = 0.067$ in six cycles. Five further cycles with anisotropic temperature coefficients reduced R to 0.050. At this stage isotropic secondary-extinction correction (Zachariasen, 1967; Larson, 1970) was applied and the weighting scheme of Cruickshank et al. (1961) was introduced. The R index was further reduced and stopped at $R = 0.038$.

The final atomic parameters are given in Table 2 and the anisotropic temperature coefficients U_{ij} in Table 3. Comparison between $|F_o|$ and $|F_c|$ values, obtained with the parameters in Tables 2 and 3, is made in Table 4. In view of the large number of the measured reflections, only the first 718 (up to $l = \pm 2$) are included in the table. The rest

Table 2. *Atomic parameters and equivalent isotropic temperature factors for the monoclinic* $Fe_2(SO_4)_3$, *with their standard deviations*

Atom	x	y	z	B
Fe(1)	0.74909(6)	0.46575(5)	0.61655(4)	0.32 Å²
Fe(2)	0.75297(6)	0.03475(6)	0.38433(4)	0.37
S(1)	0.03835(9)	0.25224(9)	0.49506(7)	0.34
S(2)	0.60408(9)	0.38148(9)	0.34898(7)	0.31
S(3)	0.60802(9)	0.11527(9)	0.64571(7)	0.34
O(1)	0.0903(3)	0.1266(3)	0.5739(2)	0.70
O(2)	−0.0604(4)	0.1894(3)	0.3998(3)	0.80
O(3)	0.1817(3)	0.3292(3)	0.4479(3)	0.67
O(4)	−0.0543(3)	0.3648(3)	0.5623(3)	0.79
O(5)	0.7121(4)	0.4793(4)	0.2805(3)	0.81
O(6)	0.4360(3)	0.4180(3)	0.3200(3)	0.67
O(7)	0.6353(3)	0.4113(3)	0.4712(2)	0.71
O(8)	0.6281(3)	0.2140(3)	0.3236(3)	0.76
O(9)	0.6335(3)	0.0024(3)	0.7384(3)	0.74
O(10)	0.7109(4)	0.0722(4)	0.5487(3)	1.03
O(11)	0.4367(3)	0.1129(3)	0.6113(3)	0.90
O(12)	0.6536(4)	0.2726(3)	0.6860(2)	0.67

Table 3. *Anisotropic temperature coefficients* U_{ij} *for monoclinic* $Fe_2(SO_4)_3$ *with their standard deviations* $(\times 10^4)$

Temperature factor
$$\exp\left[-2\pi^2\left(U_{11}h^2\,a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*\right)\right]$$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe(1)	38(3)	41(3)	43(3)	− 1(1)	0(1)	− 5(1)
Fe(2)	44(3)	43(3)	53(3)	10(1)	− 1(1)	− 3(1)
S(1)	31(4)	32(4)	65(4)	5(2)	4(2)	7(2)
S(2)	42(4)	38(4)	36(4)	5(2)	− 2(2)	3(2)
S(3)	50(4)	43(4)	39(4)	−10(2)	− 6(2)	3(2)
O(1)	84(11)	77(10)	106(12)	35(7)	1(7)	44(7)
O(2)	96(11)	116(11)	94(12)	−50(7)	−30(8)	− 5(8)
O(3)	53(10)	72(10)	131(12)	−13(6)	39(7)	18(7)
O(4)	85(11)	74(10)	143(13)	50(7)	41(8)	−30(8)
O(5)	107(11)	141(12)	61(12)	− 65(8)	8(7)	23(8)
O(6)	54(10)	113(10)	89(12)	53(7)	−15(7)	−27(7)
O(7)	101(11)	144(11)	27(11)	− 9(7)	−21(7)	−16(7)
O(8)	123(11)	43(9)	129(13)	35(7)	−41(8)	−17(7)
O(9)	131(11)	82(10)	70(12)	−23(7)	−49(8)	56(7)
O(10)	158(13)	159(12)	74(13)	−18(9)	49(8)	−39(9)
O(11)	71(11)	102(11)	171(14)	−28(7)	−43(8)	63(8)
O(12)	149(11)	35(9)	70(11)	−46(7)	7(7)	3(7)

Table 4. *Observed and calculated structure factors for monoclinic* Fe2(SO4)3

h k l	$|F_o|$	$|F_c|$
2 0 0	81.7	92.5
4	36.6	35.4
6	135.6	145.8
8	79.9	78.6
10	57.4	56.9
1 1 0	4.0	3.1
2	106.2	112.0
3	5.7	3.2
4	28.0	30.0
5	6.9	5.0
6	39.9	36.5
7	18.3	16.9
8	1.5	1.6
9	11.6	11.1
10	33.9	33.4
11	1.7	2.3
0 2 0	101.2	112.4
1	4.8	2.5
2	142.2	160.4
3	45.6	45.2
4	102.5	103.3
5	8.7	8.0
6	104.7	105.7
7	12.1	11.4
8	86.7	86.1
9	1.6	1.5
10	33.4	33.4
11	7.8	6.5
1 3 0	1.1	1.3
2	26.8	21.7
3	8.9	7.8
4	32.7	29.6
5	36.5	34.6
6	67.4	69.3
7	16.9	15.8
8	67.7	68.4
9	1.6	1.4
10	6.5	5.8
11	9.3	8.0
0 4 0	33.3	30.5
1	19.3	18.2
2	108.3	108.7
3	12.3	12.1
4	123.2	128.0
5	10.3	8.6
6	6.3	9.8
7	1.5	4.2
8	38.9	37.0
9	1.6	4.2
10	84.0	85.8
11	1.7	0.5
1 5 0	11.1	10.0
2	1.2	3.9
3	20.8	19.7
4	9.3	9.2
5	25.8	24.2
6	49.6	48.7
7	21.6	23.3
8	47.2	47.4
9	1.6	3.3
10	14.3	13.2
11	9.6	7.9
0 6 0	25.4	25.3
1	21.1	20.2
2	64.0	62.3
3	47.0	44.4
4	29.1	27.0
5	23.8	23.0
6	12.4	11.5
7	1.6	0.6
8	15.2	14.0
9	8.3	8.3
10	1.7	5.2
11	1.8	4.6
1 7 0	17.6	15.9
2	62.7	63.0
3	1.4	2.0
4	44.9	44.0
5	14.5	5.9
6	22.0	21.7
7	7.0	7.1
8	8.1	8.7
9	22.9	21.1
10	30.7	28.7
11	9.8	10.2
0 8 0	66.8	68.9
1	6.7	4.5
2	56.6	54.5
3	1.3	4.7
4	46.7	47.4
5	16.9	17.4
6	17.9	16.5
7	9.0	8.1
8	6.3	6.3
9	1.7	3.0
10	21.1	20.1
11	1.8	6.0
1 9 0	10.1	9.2
2	24.8	26.2
3	13.0	12.1
4 9 0	36.4	35.1
5	10.0	10.1
6	16.2	15.4
7	1.7	3.3
8	1.7	3.3
9	1.8	2.3
10	1.8	2.8
11	20.8	21.4
0 10 0	21.9	22.4
1	24.4	23.6
2	27.8	27.1
3	9.2	7.3
4	74.1	74.2
5	15.9	15.5
6	16.6	16.3
7	8.7	8.9
8	8.6	9.9
9	17.3	18.0
10	41.4	41.1
11	9.5	9.9
1 11 0	8.2	3.9
2	28.1	28.3
3	18.5	17.5
4	1.7	2.9
5	1.7	3.0
6	48.1	49.0
7	1.8	1.1
8	38.8	39.2
9	14.7	13.9
10	8.8	7.1
11	8.7	8.3
0 12 0	55.2	55.8
1	1.7	0.1
2	45.5	46.3
3	8.6	8.9
4	11.1	12.1
5	7.9	7.6
6	67.9	68.1
7	1.8	1.1
8	54.3	54.2
9	1.9	1.4
10	7.3	7.6
11	1.9	4.4
1 0 1	12.8	12.5
2	87.2	80.1
5	29.2	28.7
7	8.2	6.9
9	36.4	35.7
11	23.4	23.6
0 1 1	0.8	1.7
1	55.1	51.5
2	81.3	75.3
3	18.0	16.5
4	26.5	25.8
6	12.5	11.4
7	63.3	63.7
8	32.1	31.6
9	7.9	8.3
10	17.3	14.6
11	9.9	8.5
0 2 1	65.2	54.8
1	77.8	71.3
2	54.0	48.2
3	22.7	24.0
4	65.5	61.8
5	17.9	16.2
6	12.4	13.0
7	6.3	4.2
8	21.1	19.9
9	23.6	24.8
10	53.7	53.1
11	13.5	13.5
0 3 1	3.7	1.9
1	87.7	79.6
2	16.9	20.6
3	43.4	41.3
4	47.3	45.8
5	63.5	62.1
6	11.1	9.1
7	31.4	29.3
8	21.0	21.4
9	64.2	64.1
10	9.4	8.0
11	1.7	5.9
0 4 1	8.8	13.7
1	60.3	55.2
2	87.3	83.0
3	38.3	35.7
4	79.7	76.6
5	32.8	32.2
6	54.3	50.2
7	9.0	7.8
8	35.4	34.8
9	17.8	17.6
10	16.6	17.4
11	18.5	18.3
0 5 1	4.0	4.4
1	91.5	85.8
2	49.7	48.4
3 5 1	117.5	116.0
4	1.4	2.9
5	23.7	21.4
6	47.8	45.8
7	63.5	62.7
8	13.4	13.5
9	28.6	28.3
10	5.5	5.9
11	46.2	46.0
0 6 1	130.3	129.8
1	8.3	6.2
2	33.3	30.7
3	43.9	43.0
4	12.9	11.1
5	28.9	27.9
6	67.1	65.2
7	10.0	9.4
8	59.9	59.5
9	16.8	16.5
10	12.1	13.1
11	13.0	13.6
0 7 1	7.7	6.4
1	59.8	55.5
2	42.7	41.4
3	58.8	56.3
4	18.5	17.5
5	100.0	99.4
6	21.1	21.0
7	19.0	18.1
8	12.4	12.1
9	56.5	57.5
10	9.7	9.2
11	44.2	45.2
0 8 1	62.9	59.6
1	7.8	7.1
2	39.4	37.2
3	33.7	34.1
4	32.7	30.6
5	17.4	16.4
6	55.7	56.3
7	1.6	2.4
8	26.1	26.6
9	1.5	7.7
10	22.9	22.5
11	21.6	22.0
0 9 1	5.8	5.4
1	43.3	43.0
2	26.4	25.8
3	61.4	60.5
4	25.7	25.9
5	29.4	28.9
6	20.5	21.9
7	51.8	52.6
8	21.3	20.6
9	16.3	16.9
10	1.8	5.4
11	39.5	40.1
0 10 1	16.1	14.9
1	40.0	40.2
2	52.6	50.3
3	7.9	5.9
4	47.8	48.7
5	1.7	0.2
6	1.7	6.0
7	1.7	5.0
8	12.2	12.4
9	1.8	3.6
10	41.8	43.3
11	15.5	15.6
0 11 1	1.7	2.8
1	49.1	49.8
2	1.7	5.3
3	8.5	9.2
4	21.7	19.8
5	31.8	32.1
6	1.8	3.5
7	25.8	24.7
8	19.4	20.0
9	28.3	27.0
10	10.2	10.8
11	8.7	6.7
0 12 1	7.5	9.3
1	37.9	35.7
2	11.7	13.0
3	17.0	16.8
4	36.4	37.3
5	1.8	5.3
6	1.8	4.8
7	1.8	1.5
8	1.9	4.1
9	1.9	2.2
10	23.2	22.2
11	1.9	0.6
0 0 2	55.0	48.9
2	25.4	19.0
4	65.0	61.2
6	9.3	7.1
8	9.9	10.0
10	35.1	35.8
0 1 2	6.8	6.0
1 1 2	108.5	117.6
2	7.6	2.0
3	107.3	103.3
4	12.8	12.0
5	159.2	165.3
6	39.2	39.8
7	77.1	72.6
8	24.6	24.9
9	66.0	65.3
10	1.6	7.0
11	85.8	85.2
0 2 2	53.5	45.0
1	103.1	99.0
2	60.0	53.7
3	55.6	53.7
4	8.1	7.5
5	64.3	63.2
6	9.3	9.3
7	18.9	18.6
8	34.8	32.9
9	21.2	20.4
10	5.7	5.8
11	11.9	8.0
0 3 2	37.0	35.1
1	70.4	65.0
2	33.8	35.4
3	94.7	90.6
4	40.4	38.6
5	68.6	65.6
6	44.3	42.7
7	111.9	110.3
8	14.9	15.1
9	63.1	63.3
10	14.1	14.7
11	21.3	22.6
0 4 2	23.7	26.7
1	28.2	25.4
2	31.4	29.3
3	64.8	62.2
4	34.7	32.5
5	6.0	4.3
6	31.1	29.5
7	11.2	9.7
8	11.7	11.9
9	1.7	2.6
10	6.7	5.7
11	15.1	13.0
0 5 2	39.6	85.9
1	13.1	8.1
2	27.3	24.3
3	48.0	47.9
4	24.9	23.9
5	41.7	40.5
6	70.9	70.1
7	19.7	18.8
8	30.4	29.8
9	18.2	19.8
10	9.8	10.3
0 6 2	30.7	31.1
1	34.0	33.8
2	6.6	6.7
3	28.2	28.7
4	26.2	25.0
5	63.0	62.7
6	1.5	4.7
7	1.6	2.4
8	26.0	25.7
9	1.7	6.2
10	13.5	14.5
11	6.5	7.2
0 7 2	30.9	29.2
1	14.2	14.9
2	8.5	8.2
3	27.0	27.0
4	17.4	16.3
5	15.1	14.9
6	26.9	27.0
7	7.2	9.9
8	18.4	18.0
9	5.9	6.0
10	12.2	12.0
11	10.2	8.5
0 8 2	1.5	1.7
1	6.0	6.2
2	44.3	42.7
3	1.5	1.5
4	12.6	13.7
5	19.8	21.1
6	1.5	1.0
7	1.6	3.3
8	18.4	18.0
9	10.7	9.8
10	5.9	6.0
11	1.7	4.5
0 9 2	17.9	18.1
1	50.8	49.0
2	8.0	6.5
3	15.2	13.0
4	16.9	15.3
5 9 2	12.7	12.5
6	1.4	7.7
7	44.6	44.5
8	13.3	11.7
9	14.0	13.6
10	1.8	3.5
11	9.3	10.1
0 10 2	40.8	40.2
1	19.6	19.1
2	17.4	17.2
3	7.8	8.5
4	16.4	14.9
5	23.0	22.6
6	1.7	5.2
7	8.9	7.2
8	1.8	4.1
9	26.2	27.3
10	12.5	14.4
11	10.4	10.7
0 11 2	7.9	5.1
1	53.1	53.0
2	22.1	22.4
3	45.3	46.2
4	13.6	13.8
5	26.3	27.6
6	16.9	17.2
7	24.9	24.3
8	7.9	9.7
9	35.5	34.8
10	20.4	20.7
11	38.5	38.7
0 12 2	21.6	20.2
1	22.5	20.8
2	10.4	11.3
3	13.5	13.2
4	11.5	11.4
5	15.4	15.6
6	9.5	9.9
7	1.8	0.9
8	1.8	4.5
9	1.9	4.4
10	1.9	5.3
11	1.9	2.3
1 0 -1	3.3	3.0
3	79.2	76.9
5	69.2	69.3
7	32.6	30.7
9	59.6	60.7
11	10.4	11.8
1 1 -1	56.1	54.8
2	76.4	72.8
3	3.6	3.0
4	9.3	8.4
5	35.6	35.1
6	40.2	39.7
7	64.8	65.2
8	34.5	33.8
9	11.3	10.8
10	31.2	30.6
11	7.9	3.7
1 2 -1	75.1	69.6
2	66.7	63.3
3	63.7	61.9
4	94.2	95.5
5	14.8	14.0
6	14.2	17.9
7	29.4	28.4
8	6.0	2.9
9	9.9	9.5
10	48.9	48.8
11	16.0	15.5
1 3 -1	117.1	120.9
2	29.1	24.7
3	39.9	38.0
4	36.6	34.0
5	59.6	57.3
6	31.2	27.8
7	43.4	41.0
8	11.3	9.8
9	38.1	37.9
10	6.5	7.2
11	14.4	13.9
1 4 -1	48.3	44.3
2	67.6	63.7
3	9.7	8.4
4	70.7	68.3
5	7.3	9.5
6	15.4	14.7
7	1.5	1.0
8	39.5	38.2
9	10.7	9.8
10	40.3	40.1
11	1.7	4.5
1 5 -1	89.2	85.3
2	16.1	15.5
3	107.7	108.3
4	17.6	17.4
5	26.1	23.6
6	45.6	44.1
7 5 -1	65.7	64.5
8	25.4	26.3
9	17.9	18.4
10	25.2	23.1
11	47.7	46.8
1 6 -1	21.1	18.8
2	60.4	56.7
3	45.6	44.5
4	9.5	13.0
5	5.5	3.6
6	85.6	85.7
7	1.6	1.1
8	65.5	65.3
9	1.7	4.0
10	17.3	17.6
11	11.4	12.8
1 7 -1	52.1	48.7
2	57.2	56.4
3	66.6	63.8
4	106.0	106.3
5	17.9	17.7
6	6.0	5.9
7	1.6	2.1
8	55.4	56.6
9	1.7	3.6
10	48.8	48.1
1 8 -1	5.5	5.7
2	37.1	35.9
3	27.5	28.1
4	58.9	57.6
5	37.0	37.6
6	65.8	65.6
7	1.6	2.7
8	46.4	46.9
9	35.6	35.3
10	29.9	29.8
11	20.7	21.3
1 9 -1	46.2	44.9
2	27.4	27.3
3	60.5	59.2
4	8.8	8.2
5	30.4	30.3
6	24.9	25.2
7	61.5	62.9
8	27.0	25.8
9	20.2	20.9
10	13.0	14.4
11	29.6	30.7
1 10 -1	39.3	38.9
2	37.9	37.8
3	1.6	5.3
4	52.5	53.3
5	12.1	11.8
6	13.6	15.0
7	7.5	8.9
8	22.9	21.7
9	1.8	3.3
10	53.1	52.9
11	10.6	10.4
1 11 -1	49.0	48.3
2	13.7	12.3
3	5.8	5.2
4	7.5	6.7
5	40.4	39.7
6	10.2	9.4
7	23.0	22.5
8	9.7	8.9
9	37.6	37.8
10	6.5	5.4
11	1.9	2.8
1 12 -1	13.7	13.4
2	23.3	22.7
3	7.3	7.8
4	32.6	33.1
5	8.2	5.4
6	19.9	19.5
7	8.6	8.4
8	10.6	10.4
9	1.9	3.7
10	16.8	16.9
11	1.9	2.8
2 0 -2	37.3	31.4
4	66.7	66.2
6	1.3	2.2
8	37.7	36.2
10	23.9	24.4
1 1 -2	104.0	117.4
2	3.3	1.0
3	115.4	121.6
4	6.4	6.3
5	105.5	106.1
6	45.6	45.5
1 2 -2	94.9	94.7
2	46.2	40.6

Table 4. *(Continued)*

h k l	$\|F_o\|$	$\|F_c\|$	h k l	$\|F_o\|$	$\|F_c\|$	h k l	$\|F_o\|$	$\|F_c\|$	h k l	$\|F_o\|$	$\|F_c\|$	h k l	$\|F_o\|$	$\|F_c\|$	h k l	$\|F_o\|$	$\|F_c\|$
3 2 -2	57.3	60.2	1 4 -2	38.2	36.1	10 5 -2	10.7	11.2	8 7 -2	27.4	27.7	6 9 -2	20.8	20.2	4 11 -2	14.8	14.4
4	23.9	22.6	2	49.1	46.8	11	1.7	3.1	9	1.7	1.6	7	54.2	53.7	5	36.1	35.8
5	50.4	51.1	3	15.6	13.1	1 6 -2	71.6	72.3	10	17.0	16.5	8	28.3	27.0	6	14.6	13.7
6	1.4	3.9	4	38.4	36.6	2	22.0	23.6	11	12.0	10.9	9	1.5	5.7	7	41.8	40.8
7	35.5	34.3	5	11.2	10.3	3	22.6	21.4	1 8 -2	29.3	27.3	10	16.0	16.2	8	1.8	2.9
8	16.9	16.2	6	7.9	6.7	4	1.4	2.3	2	34.3	33.1	11	8.7	8.2	9	41.2	41.6
9	35.1	35.1	7	9.5	9.7	5	39.7	39.1	3	1.5	1.7	1 10 -2	22.2	20.4	10	10.2	10.1
10	17.0	16.6	8	7.2	8.1	6	14.3	13.4	4	10.2	10.1	2	14.0	13.5	1 12 -2	22.9	23.0
11	1.7	5.5	9	15.8	16.7	7	17.7	18.3	5	23.5	22.7	3	9.6	9.0	2	16.6	16.7
1 3 -2	93.5	92.0	10	11.8	11.2	8	1.6	2.4	6	22.8	22.7	4	1.7	2.6	3	9.8	8.7
2	4.7	5.6	11	11.1	10.1	9	19.7	20.6	7	10.3	9.5	5	21.6	22.7	4	1.5	7.4
3	105.7	106.8	1 5 -2	103.7	104.6	10	14.8	15.5	8	13.6	13.4	6	1.7	3.8	5	23.6	23.7
4	43.0	41.3	2	38.7	38.2	11	9.2	7.7	9	1.7	4.3	7	7.6	6.5	6	1.8	7.6
5	65.3	62.6	3	5.0	3.9	1 7	7.9	8.7	10	19.4	19.5	8	1.8	2.9	7	1.8	2.0
6	18.5	17.8	4	43.9	44.1	2	1.4	0.2	11	12.0	13.8	9	16.4	16.0	8	1.8	2.1
7	91.3	91.1	5	4.8	7.7	3	30.2	29.5	1 9 -2	43.5	42.2	10	1.8	2.7	9	15.5	14.8
8	11.0	10.1	6	17.0	14.8	4	25.6	25.4	2	16.5	17.6	11	13.4	13.6	10	1.9	1.9
9	42.8	42.5	7	77.3	77.4	5	15.7	15.4	3	12.3	12.3	1 11 -2	36.7	35.6	11	1.9	1.6
10	16.6	16.5	8	14.5	15.2	6	32.8	32.4	4	27.7	27.8	2	34.6	34.4			
11	21.9	23.2	9	28.2	27.8	7	13.3	13.5	5	20.6	18.4	3	44.9	44.4			

Table 5

Interatomic distances in monoclinic Fe₂(SO₄)₃ *with their standard deviations*

S(1)O₄ tetrahedron

S(1)—O(1)	1.470 Å	O(1)—O(2)	2.424 Å
O(2)	1.472	O(3)	2.395
O(3)	1.468	O(4)	2.358
O(4)	1.461	O(2)—O(3)	2.393
		O(4)	2.413
Average S(1)—O	1.468(3)	O(3)—O(4)	2.397
		Average O—O	2.397(4)

S(2)O₄ tetrahedron

S(2)—O(5)	1.470 Å	O(5)—O(6)	2.402 Å
O(6)	1.462	O(7)	2.388
O(7)	1.463	O(8)	2.420
O(8)	1.468	O(6)—O(7)	2.397
		O(8)	2.354
Average S(2)—O	1.466(3)	O(7)—O(8)	2.401
		Average O—O	2.394(4)

S(3)O₄ tetrahedron

S(3)—O(9)	1.462 Å	O(9)—O(10)	2.381 Å
O(10)	1.468	O(11)	2.382
O(11)	1.467	O(12)	2.394
O(12)	1.467	O(10)—O(11)	2.415
		O(12)	2.391
Average S(3)—O	1.466(3)	O(11)—O(12)	2.401
		Average O—O	2.394(4)

Table 5. (Continued)

Fe(1)O$_6$ octahedron

Fe(1)—O'(3)	1.991 Å	O'(3)—O'(4)	2.821 Å
O'(4)	1.960	O'(6)	2.710
O'(6)	1.980	O (7)	2.839
O (7)	1.981	O'(9)	2.854
O'(9)	1.962	O'(4)—O (7)	2.803
O (12)	2.005	O'(9)	2.686
		O (12)	2.942
Average Fe(1)—O	1.980(3)	O'(6)—O (7)	2.901
		O'(9)	2.761
		O(12)	2.746
		O (12)—O (7)	2.766
		O'(9)	2.776
		Average O—O	2.800(4)

Fe(2)O$_6$ octahedron

Fe(2)—O'(1)	1.952 Å	O'(1)—O'(2)	2.724 Å
O'(2)	2.040	O'(5)	2.751
O'(5)	1.999	O (10)	2.774
O (8)	1.978	O'(11)	2.910
O (10)	1.974	O'(2)—O'(5)	3.020
O'(11)	2.024	O (8)	2.731
		O (10)	2.778
Average Fe(2)—O	1.994(3)	O (8)—O'(5)	2.698
		O'(10)	2.961
		O'(11)	2.952
		O'(11)—O'(5)	2.842
		O (10)	2.720
		Average O—O	2.822(4)

are available on request. Interatomic distances and bond angles are given in Tables 5 and 6, in which the indices in parentheses refer to the atoms in Fig. 2.

Description of the structure and discussion

As already mentioned, all the atoms in the unit cell are in general position 4c. Figure 1 is a projection of the structure parallel to b. It can easily be seen that half the Fe atoms in the unit cell lie very nearly on a yz plane at x = 0.25 and the other half on the parallel plane at

Table 6. *Bond angles in the monoclinic* Fe$_2$(SO$_4$)$_3$ *with their standard deviations*

S(1)O$_4$ tetrahedron			Fe(1)O$_6$ octahedron		
O(1)—S(1)—O(2)		110.94°	O'(3)—Fe(1)—O'(4)		91.13°
	O(3)	109.21		O'(6)	86.05
	O(4)	107.12		O (7)	91.24
O(2)—S(1)—O(3)		109.00		O'(9)	92.45
	O(4)	110.72	O'(4)—Fe(1)—O (7)		90.68
O(3)—S(1)—O(4)		109.82		O'(9)	86.45
				O(12)	95.82
Average		109.47(16)	O'(6)—Fe(1)—O (7)		94.15
				O'(9)	88.91
				O (12)	87.09
S(2)O$_4$ tetrahedron			O (12)—Fe(1)—O (7)		87.87
				O'(9)	88.81
O(5)—S(2)—O(6)		109.99°			
	O(7)	108.97	Average		90.05(11)
	O(8)	110.91			
O(6)—S(2)—O(7)		110.03			
	O(8)	106.93	Fe(2)O$_6$ octahedron		
O(7)—S(2)—O(8)		109.99			
			O'(1)—Fe(2)—O'(2)		86.00°
Average		109.47(16)		O'(5)	88.28
				O (10)	89.90
				O'(11)	94.08
S(3)O$_4$ tetrahedron			O'(2)—Fe(2)—O'(5)		96.78
				O (8)	85.63
				O (10)	87.57
O(9)—S(3)—O(10)		108.74°	O (8)—Fe(2)—O'(5)		85.44
	O(11)	108.83		O (10)	97.06
	O(12)	109.68		O'(11)	95.08
O(10)—S(3)—O(11)		110.72	O'(11)—Fe(2)—O'(5)		89.91
	O(12)	109.05		O (10)	85.74
O(11)—S(3)—O(12)		109.82			
Average		109.47(17)	Average		90.12(12)

$x = 0.75$. Although the oxygen atoms form some densely populated planes, *e.g.* parallel to (403), (10$\bar{1}$) or (40$\bar{1}$), yet the arrangement is far from a close-packing.

The structure may better be visualized in terms of the coordination polyhedra around the cations. As shown in the clinographic projection of the structure, Fig. 2, there are three different SO$_4$ tetrahedra and two different FeO$_6$ octahedra in the asymmetric unit of the cell. All the coordination polyhedra are isolated. The tetrahedra share each of their vertices with a vertex of an FeO$_6$ octahedron, thus forming
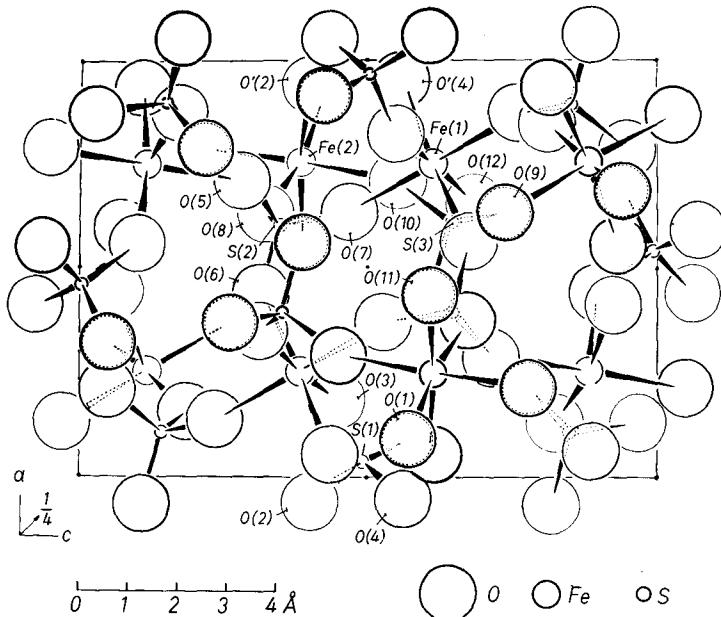
Fig. 1. Projection of the structure parallel to b. Atoms with greater y are indicated with heavier circles. In case of atoms differing by one b translation the lower atom is shown as a dashed circle

a three-dimensional network of tetrahedra and octahedra in which each O atom is bonded to only one S and one Fe atom. Within the three-dimensional network of $Fe_2(SO_4)_3$ are distinguished nonplanar, eight-membered rings of the form:
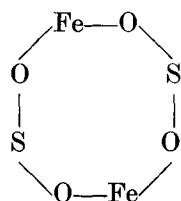
The majority of the rings are strongly distorted.

In Fig. 3 are shown the coordination polyhedra around the cations, with the correponding interatomic distances. All the SO_4 tetrahedra are almost regular with virtually equal S—O distances. The average S—O distances in the three tetrahedra are 1.468, 1.466 and 1.466 Å and the corresponding average O—O distances are 2.397, 2.394 and
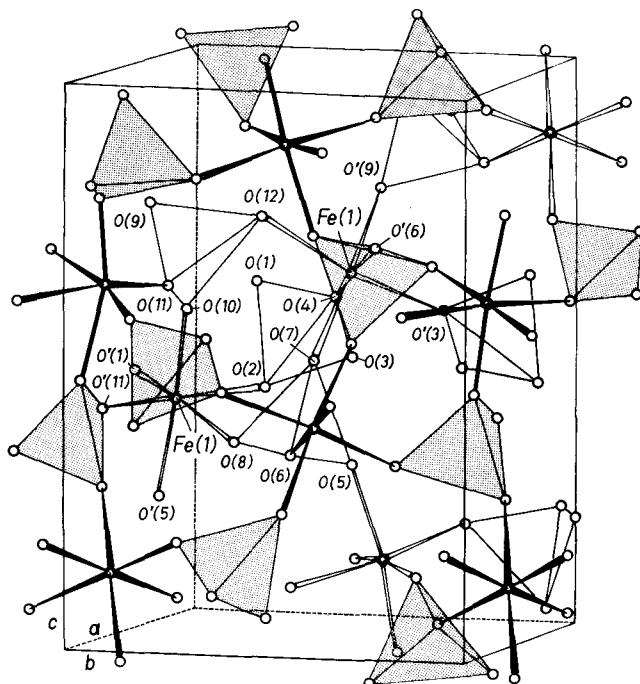
Fig. 2. Clinographic projection of the monoclinic $Fe_2(SO_4)_3$. SO_4 tetrahedra, at various heights in x, are differently shaded

2.394 Å. The tetrahedral bond angles are very near their ideal value 109.46° with deviations not exceeding 2.5°. These values compare excellently with those known for the SO_4 tetrahedra of other sulfates.

The two FeO_6 octahedra are also only slightly distorted. The average Fe—O distances are 1.980 Å for $Fe(1)O_6$ and 1.994 Å for $Fe(2)O_6$, whereas the corresponding average O—O distances are 2.800 Å and 2.822 Å. The bond angles differ from their ideal value 90° by less than 7°.

The Fe—O and O—O distances agree very well with the values known from other compounds with Fe^{3+} ions. However, owing to the fact that the FeO_6 octahedra do not share any edges or faces with other polyhedra, there are not any pronounced differences in the Fe—O distances and the octahedra appear only very little distorted. For comparison, the case of hematite, α Fe_2O_3 (BLAKE et al., 1966), may be mentioned, where each FeO_6 octahedron shares three edges and one face with other octahedra; in that structure the Fe—O distances fall
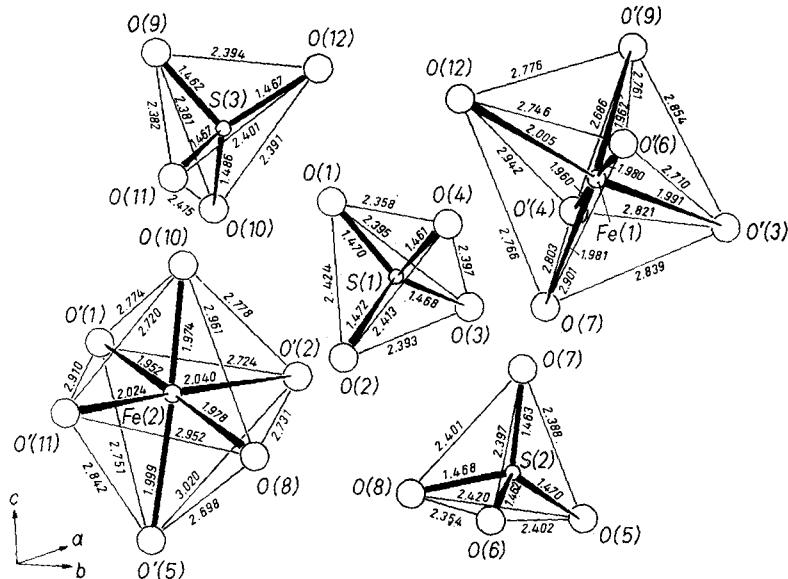
Fig. 3. Clinographic projections of the coordination polyhedra around the cations, shown apart from one another. The orientations of the polyhedra are for the cations shown in Fig. 2

into two groups with 1.945 Å and 2.116 Å respectively. The corresponding deviations of the octahedral angles from the ideal value 90° are, naturally, much larger than in $Fe_2(SO_4)_3$.

Acknowledgments

We thank Prof. P. A. KOKKOROS for putting the material of his investigation on $Fe_2(SO_4)_3$ at our disposal. Thanks are due to the University of Thessaloniki for the use of its UNIVAC 1106 computer and the Nuclear Research Center "Democritus", Athens, Greece, for the use of its CDC 3300 computer.

References

R. L. BLAKE, R. E. HESSEVICK, T. ZOLTAI and L. W. FINGER (1966), Refinement of the hematite structure. Amer. Mineral. **51**, 123—129.

P. C. CHRISTIDIS and P. J. RENTZEPERIS (1975), The crystal structure of rhombohedral $Fe_2(SO_4)_3$. Z. Kristallogr. **141** [in press].

D. W. J. CRUICKSHANK, D. E. PILLING, A. BUJOSA, F. M. LOVELL and M. R. TRUTER (1961), Crystallographic calculations on the Ferranti Pegasus and Mark I computers. In: *Computing methods and the phase problem in x-ray crystal analysis*. Pergamon Press, New York, pp. 45—56.

GMELIN, *Handbuch der anorganischen Chemie* (1930), vol. **59** B, pp. 439—446. Verlag Chemie, Berlin.

W. C. HAMILTON (1955), On the treatment of unobserved reflections in the least-squares adjustment of crystal structures. Acta Crystallogr. **8**, 185—186.

International tables for x-ray crystallography, Vol. III (1968) pp. 204—205 and 215.

R. W. JAMES and G. W. BRINDLEY (1931), Some numerical values of the atomic scattering factor. Z. Kristallogr. **78**, 470—476.

P. A. KOKKOROS (1965), Röntgenuntersuchung der wasserfreien Sulfate der dreiwertigen Metalle Eisen, Chrom und Gallium. Tschermaks min. petr. Mitt. **10**, 45—51.

A. C. LARSON (1970), The inclusion of secondary extinction in least squares refinement of crystal structures. In: *Proceedings of the Intern. Summer School on Crystallographic Computing*, Ottawa, edited by F. R. AHMED, pp. 291—294. Munksgaard, Copenhagen.

J. W. MELLOR (1953), *A comprehensive treatise on inorganic and theoretical chemistry*, Vol. XIV, pp. 302—316. Longmans, London.

J. STEWART, G. KRUGER, H. AMMON, C. DICKINSON and S. HALL (1972), *The X-ray System of crystallographic programs for any computer*. Technical Report 192, Computer Science Center, University of Maryland.

W. H. ZACHARIASEN (1967), A general theory of x-ray diffraction in crystals. Acta Crystallogr. **23**, 558—564.