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The crystal structure of rhombohedral $Fe_2(SO_4)_3$

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Auszug

Die Kristallstruktur des rhomboedrischen $Fe_2(SO_4)_3$ wurde mit Hilfe dreidimensionaler Diffraktometer-Daten (Philips PW 1100) bestimmt. Die Struktur wurde mittels direkter Phasenbestimmung und Differenz-Fouriersynthesen ermittelt. Die Gitterkonstanten, bezogen auf das hexagonale Achsensystem und ermittelt nach der Methode der kleinsten Quadrate aus direkt auf dem Diffraktometer gemessenen θ-Werten, sind: $a = 8{,}2362$ Å, $c = 22{,}1786$ Å; $Z = 6$, Raumgruppe $R\bar{3}$. Die entsprechenden Gitterkonstanten für die primitive rhomboedrische Zelle sind: $a_{rh} = 8{,}7901$ Å, $\alpha_{rh} = 55{,}87°$, $Z = 2$. Atomparameter und anisotrope Temperaturfaktoren wurden nach der Methode der kleinsten Quadrate bis zu $R = 0{,}057$ verfeinert. Korrekturen für anomale Dispersion und sekundäre Extinktion wurden berücksichtigt.

In der asymmetrischen Einheit der Elementarzelle befindet sich nur ein fast regelmäßiges SO_4-Tetraeder. Die S—O-Abstände sind praktisch gleich dem mittlerem Wert 1,465 Å. Die entsprechenden mittleren O—O-Abstände sind 2,393 Å, und die tetraedrischen Valenzwinkel weichen vom Idealwert 109,46° weniger als 1,9° 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 1,981 Å bzw. 1,988 Å; die entsprechenden mittleren O—O-Abstände sind 2,803 Å bzw. 2,812 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 je einem S- und einem Fe-Atom verbunden ist. Die Struktur ähnelt im wesentlichen derjenigen der monoklinen Modifikation von $Fe_2(SO_4)_3$.

Abstract

The crystal structure of the rhombohedral $Fe_2(SO_4)_3$ has been determined using three-dimensional x-ray diffraction intensities, measured with an automated Philips PW 1100 single-crystal diffractometer. The structure was solved by direct phase determination combined with difference-Fourier syntheses. The hexagonal unit-cell constants, obtained by least-squares from direct θ-value measurements on the diffractometer, are $a = 8.2362$ Å, $c = 22.1786$ Å,

Z = 6; space group $R\bar{3}$. The constants corresponding to the primitive rhombohedral *cell* are: $a_{rh} = 8.7901$ Å, $\alpha_{rh} = 55.87°$, $Z = 2$. Atomic parameters and anisotropic temperature factors were refined by least squares to $R = 0.057$. Corrections for anomalous dispersion and secondary extinction were applied.

There is only one, almost regular SO_4 tetrahedron in the asymmetric unit of the cell. The S—O distances are virtually equal, their average value being 1.465 Å. The corresponding average O—O distance is 2.393 Å and the tetrahedral bond angles deviate from the ideal value 109.46° by less than 1.9°. The two Fe atoms in the asymmetric unit are octahedrally coordinated. Both FeO_6 octahedra are only slightly distorted. The average Fe—O distances in the two octahedra are 1.981 Å and 1.988 Å respectively, whereas the corresponding average O—O distances are 2.803 Å and 2.812 Å.

All the coordination polyhedra are isolated. The SO_4 tetrahedra share each of their vertices with an 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. The structure resembles, in a general way, that of the monoclinic modification of $Fe_2(SO_4)_3$.

Introduction

In a recent publication on the structure of the monoclinic $Fe_2(SO_4)_3$ (CHRISTIDIS and RENTZEPERIS, 1975), reference was made to its rhombohedral modification and also to the previous work by KOKKOROS (1965). Further on, a detailed description of the method of preparation of both modifications was given. In what follows the structure of the rhombohedral $Fe_2(SO_4)_3$ is described in detail and compared to that of the monoclinic modification.

Experimental

A perfectly developed, transparent rhombohedron was selected and shaped into a small sphere 0.33 mm in diameter in a Nonius sphere-grinder. To avoid 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 PH (*"peak hunting"*) routine and then the LAT (*"lattice constants"*) routine of the instrument. To obtain greater accuracy, the intensity distribution of 82 strong reflections with large 2θ values was measured by an automatic step-scanning process. It was thus possible to have the diffractometer centered exactly on the Ka_1 peaks, (Mo radiation) and to measure the corresponding θ angles, taking advantage of the high accuracy of the ω circle of the diffractometer. The θ-values obtained were used in the least-squares program PARAM (part of the *"X-ray system of crystallographic programs"*, STEWART

Table 1. *Unit-cell data for the rhombohedral* $Fe_2(SO_4)_3$
(standard errors, given in parentheses, refer to the last digit)

	This investigation	Kokkoros (1965)		This investigation	Kokkoros (1965)
	Rhombohedral axes			Hexagonal axes	
a_{rh}	8.7901(3) Å	8.791(4) Å	a_h	8.2362(2) Å	8.236(2) Å
α_{rh}	55.87°(5)	55.86°(3)	c_h	22.1786(10)	22.18(2)
V_{rh}	434.307 Å^3	434.29 Å^3	V_h	1302.922 Å^3	1302.94 Å^3
Z	2	2	Z	6	6

$\varrho_{meas} = 3.06$ g · cm^{-3} (Kokkoros, 1965).
$\varrho_{calc} = 3.057$ g · cm^{-3}.
Space group: $R\bar{3}$.

et al., 1972). The final values obtained are given in Table 1, together with those of Kokkoros (1965) for comparison. The agreement is excellent.

Systematic absences led to the two space groups $R3$ and $R\bar{3}$. As statistical treatment of the measured intensities could not clearly differenciate between them, the centrosymmetrical space group $R\bar{3}$, which seemed more probable (see also Kokkoros, 1965), was tried first. It turned out to be the right one for the rhombohedral modification.

Three-dimensional intensity data over one hemisphere of the reciprocal lattice were collected on the diffractometer in the ω-scan mode, using Mo$K\alpha$ radiation, monochromated with a graphite monochromator. All symmetrical reflections were measured and then reduced to 2361 independent ones. 238 of these 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 was applied ($\mu = 41.86$ cm^{-1}). For all the 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 obtained by combining direct phase determination with difference Fourier syntheses. Using the program "PHASE" of the *X-ray system of crystallographic programs*, the phases of 105 strong reflections were determined, which were further used to obtain

an E map. The map contained all necessary information about the structure but, due to the many spurious peaks, it proved difficult to unambiguously assign specific atoms to certain maxima. Finally eight peaks were found on the threefold axis; these appeared to be candidate peaks for the two Fe atoms of the asymmetric unit. By critical elimination, and taking into account that the Fe atoms should be octahedrally coordinated by O atoms, two peaks at heights 11/72 and 25/72 were chosen as most probable for Fe locations. Using these positions of the Fe atoms, a ΔF Fourier map was obtained, which showed a prominent peak at (7/24, 7/24, 18/72). The peak appeared also on the E map and was identified as a S atom position. With these positions for Fe and S, a structure-factor calculation was carried out, which gave $R = 0.30$. The positions of the O atoms were then easily found by successive Fourier and difference-Fourier syntheses. Structure factor calculation with all atoms included gave $R = 0.254$.

Refinement of the structure was carried out by least squares, using the program CRYLSQ of the "*X-ray system*". All the atoms were assumed to be in the fully ionized state and probable isotropic temperature factors were assigned to them. Atomic form factors and anomalous dispersion corrections for Fe^{3+} were obtained from the *International tables* (LONSDALE, 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 the refinement went down to $R = 0.101$ in four cycles. Further cycles with anisotropic temperature coefficients reduced R to 0.071. Corrections for isotropic secondary extinction (ZACHARIASEN, 1967; LARSON, 1970) were then applied. Also the weighting scheme of CRUICKSHANK *et al.* (1961) was introduced, specifically $w = (a + F_o + cF_o^2)^{-1}$ with $a = 50$ and

Table 2. *Atomic parameters for hexagonal axes, and equivalent isotropic temperature factors B of rhombohedral* $Fe_2(SO_4)_3$, *with their standard deviations*

Atom	x	y	z	B
Fe(1)	0	0	0.14411(2)	0.27 Å^2
Fe(2)	0	0	0.35070(2)	0.31
S	0.29044(7)	0.28818(8)	0.25072(2)	0.27
O(1)	0.1943(3)	0.2048(3)	0.19382(10)	0.65
O(2)	0.2240(3)	0.1456(3)	0.29843(11)	0.74
O(3)	0.4922(3)	0.3634(3)	0.24358(9)	0.42
O(4)	0.2527(3)	0.4393(3)	0.26590(11)	0.64

Table 3. *Atomic parameters for rhombohedral axes, for rhombohedral* $Fe_2(SO_4)_3$, *with their standard deviations*

Atom	x	y	z
Fe(1)	0.14411(2)	0.14411(2)	0.14411(2)
Fe(2)	0.35070(2)	0.35070(2)	0.35070(2)
S	0.54116(7)	0.24846(11)	−0.03746(8)
O(1)	0.3881(3)	0.2043(5)	−0.0109(4)
O(2)	0.5224(4)	0.2201(5)	0.1528(4)
O(3)	0.7358(3)	0.1148(4)	−0.1198(3)
O(4)	0.5186(3)	0.4525(5)	−0.1734(3)

Table 4. *Anisotropic temperature coefficients* U_{ij} *of rhombohedral* $Fe_2(SO_4)_3$ *with their standard deviations*

Temperature factor for hexagonal axes:

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

The Fe atoms on the threefold axis have their parameters constrained so that $U_{11} = U_{22} = 2U_{12}$ and $U_{13} = U_{23} = 0$

Atom	U_{11}	U_{22}	U_{33}
Fe(1)	0.00437(16)	0.00437(16)	0.00266(16)
Fe(2)	0.00426(16)	0.00426(16)	0.00339(16)
S	0.00321(16)	0.00354(16)	0 00357(17)
O(1)	0.0085(7)	0.0094(7)	0.0066(7)
O(2)	0.0084(7)	0.0101(8)	0.0098(7)
O(3)	0.0016(5)	0.0073(6)	0.0070(6)
O(4)	0.0075(7)	0.0052(6)	0.0117(8)

Atom	U_{12}	U_{13}	U_{23}
Fe(1)	0.00218(16)	0	0
Fe(2)	0.00215(16)	0	0
S	0.00118(13)	0.00039(13)	−0.00120(12)
O(1)	0.0026(6)	−0.0050(6)	−0.0072(6)
O(2)	0.0043(6)	0.0071(6)	0.0082(6)
O(3)	0.0014(5)	0.0026(5)	−0.0010(5)
O(4)	0.0051(6)	−0.0023(6)	−0.0052(6)

$c = 0.01$. The discrepancy index was further reduced and stopped at $R = 0.057$.

The final atomic parameters referring to both hexagonal and rhombohedral axes are given in Tables 2 and 3. Table 4 shows the anisotropic temperature coefficients U_{ij}. Comparison between $|F_o|$ and

Table 5. *Observed and calculated structure factors for the rhombohedral* $Fe_2(SO_4)_3$

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	$\|F_o\|$	$\|F_c\|$
-13	14	6	26.4	22.3	-7	10	1	2.5	3.3	-4	8	6	132.1	127.0	-2	14	5	2.9	5.3	1	2	1	1.6	5.4
		9	3.0	9.0			4	14.8	17.3			9	2.4	7.2			8	17.9	18.7			5	28.7	18.6
-13	15	2	3.0	8.2			7	12.4	12.4	-4	9	2	2.4	7.5	-2	15	1	50.7	58.9			8	143.2	136.8
-12	13	2	2.7	13.4			10	166.2	173.9			5	89.0	82.8			4	59.1	64.0	1	3	1	30.2	24.1
		5	47.6	49.0	-7	11	3	22.1	17.6			8	17.5	16.1	-1	2	3	183.1	196.9			4	164.7	181.0
		8	25.4	29.0			6	16.9	17.7	-4	10	1	2.5	8.1			5	190.3	196.1			7	78.6	64.9
-12	14	1	2.9	4.7			9	23.3	18.1			4	85.2	80.3			9	103.8	87.6			10	192.0	198.4
		4	63.2	62.7	-7	12	2	25.8	25.7			7	18.8	10.8	-1	3	2	10.3	5.8	1	4	0	221.3	248.9
		7	2.9	5.6			5	18.1	18.3			10	115.4	119.5			5	68.7	54.6			3	65.7	61.0
		10	49.8	49.6			8	35.9	32.4	-4	11	3	29.6	24.1			8	106.3	91.9			6	106.9	108.0
-12	15	3	31.6	34.2	-7	13	1	35.3	33.4			6	21.1	17.1	-1	4	1	40.0	31.7			9	87.0	81.2
		6	66.0	66.9			4	47.3	47.2			9	15.9	11.9			4	100.8	105.8	1	5	2	7.7	13.5
		9	36.1	36.1			7	13.0	14.0	-4	12	2	34.7	31.3			7	151.1	142.0			5	75.4	73.4
-11	12	1	47.6	44.4			10	100.9	103.3			8	12.8	14.3			10	232.1	245.6			8	17.4	16.2
		4	102.4	104.9	-7	14	3	20.9	19.7	-4	13	1	34.3	32.1	-1	5	5	1.7	7.3	1	6	1	30.7	24.0
		7	22.5	21.1			6	2.9	15.7			4	76.1	76.5			6	154.5	166.6			4	125.5	120.0
		10	52.5	52.4			9	22.8	24.0			7	37.2	36.5			9	38.4	35.4			7	14.7	9.7
-11	13	3	39.0	36.9	-7	15	2	17.8	19.7			10	85.8	88.5	-1	6	2	9.9	13.5			10	160.6	172.5
		6	61.5	58.8			5	12.5	14.1	-4	14	3	13.8	13.8			5	102.1	103.0	1	7	0	100.2	97.2
		9	19.7	20.8			8	25.5	26.1			6	2.9	15.3			8	13.3	14.2			3	30.6	23.4
-11	14	2	49.0	49.1	-7	16	1	11.7	14.5			9	2.9	4.0	-1	7	1	23.1	20.6			6	130.5	133.9
		8	53.6	53.0			4	64.1	69.4	-4	15	2	23.6	24.0			4	47.9	47.3			9	13.1	13.9
-11	15	1	2.9	2.9			7	18.3	23.3			5	27.2	30.3			7	2.3	1.2	1	8	2	37.9	35.2
		4	19.5	16.7	-6	7	2	75.9	68.5			8	31.9	32.9			10	160.4	170.2			5	81.8	76.8
		7	3.0	10.7			5	24.8	20.5	-3	4	2	115.9	107.9	-1	8	3	60.6	52.6			8	12.5	12.0
		10	83.6	89.4			8	108.1	98.0			5	20.7	15.2			6	66.6	62.6	1	9	1	59.7	52.7
-10	11	3	2.7	1.8	-6	8	1	106.0	98.3			8	142.9	136.8			9	11.1	10.0			4	77.5	76.9
		6	51.7	52.0			4	99.9	96.0	-3	5	1	37.3	36.9	-1	9	2	26.6	21.8			7	38.8	33.5
		9	39.9	38.5			7	92.1	86.8			4	194.7	215.7			5	78.4	76.1			10	88.0	91.2
-10	12	2	18.8	18.8			10	120.6	114.9			7	34.3	31.9			8	31.0	25.7	1	10	0	126.3	129.4
		5	2.8	4.5	-6	9	3	35.8	33.8			10	63.2	56.6	-1	10	1	47.1	41.3			3	28.6	26.1
		8	17.1	17.5			6	105.7	99.4	-3	6	3	15.7	11.6			4	94.0	94.8			6	11.8	13.4
-10	13	1	19.7	20.7			9	51.8	47.7			6	79.6	66.0			7	51.4	45.5			9	17.6	16.3
		4	19.4	21.9	-6	10	2	94.9	90.0			9	14.5	5.2			10	58.2	57.9	1	11	2	19.9	18.3
		7	2.9	5.2			5	10.6	7.6	-3	7	2	151.3	157.2	-1	11	3	53.4	49.1			5	28.4	27.6
		10	112.4	117.8			8	78.2	75.3			5	30.0	24.7			6	68.6	68.5			8	14.0	17.6
-10	14	3	21.8	24.0	-6	11	1	43.7	41.4			8	181.3	195.0			9	51.7	48.7	1	12	1	46.3	47.5
		6	2.9	14.5			4	107.7	107.0	-3	8	1	40.8	38.7	-1	12	2	16.2	15.8			4	88.2	94.2
		9	2.9	2.2			7	43.6	39.8			4	145.3	148.7			5	49.8	47.5			7	29.3	29.3
-10	15	2	2.9	7.2			10	51.2	53.8			7	61.2	56.2			8	31.3	30.9			10	52.4	55.0
		5	26.7	29.4	-6	12	3	87.5	82.5			10	122.8	120.2	-1	13	1	58.3	58.6	1	13	0	93.0	101.0
		8	2.9	7.9			6	86.6	84.9	-3	9	3	8.4	8.3			4	88.7	92.0			3	31.1	32.1
-10	16	1	15.9	17.5			9	87.0	85.3			6	86.5	81.7			7	43.2	45.7			6	28.0	28.5
		4	65.2	74.4	-6	13	2	49.6	48.0			9	83.6	76.6			10	41.7	42.8			9	28.0	34.4
		7	2.7	15.1			5	12.7	11.0	-3	10	2	108.7	107.7	-1	14	3	2.9	1.6	2	0	2	12.4	7.5
-9	10	2	26.8	24.8			8	74.0	73.4			5	39.1	35.1			6	29.2	28.5			5	33.1	25.4
		5	56.5	51.1	-6	14	1	2.9	10.9			8	123.4	127.1			9	3.1	5.8			8	102.9	91.0
		8	48.3	45.8			4	32.4	32.1	-3	11	1	30.2	28.0	0	0	6	131.1	116.0	2	1	1	120.4	110.1
-9	11	1	93.5	88.2			7	16.0	15.9			4	75.0	72.6			9	71.3	55.8			4	163.1	169.7
		4	150.0	152.2			10	96.1	98.5			7	11.2	8.9	0	1	2	124.2	134.1			7	125.6	110.9
		7	80.0	73.8	-6	15	3	33.6	36.5			10	110.7	112.9			5	33.0	25.1			10	220.0	225.3
		10	54.9	56.8			6	78.1	79.8	-3	12	3	40.1	39.6			8	59.4	49.9	2	2	0	77.5	75.5
-9	12	3	47.4	45.6			9	33.0	33.4			6	115.2	118.8	0	2	1	10.2	8.4			3	8.7	6.8
		6	90.4	90.4	-6	16	2	30.8	34.8			9	54.4	50.8			4	203.2	225.3			6	197.1	210.2
		9	50.2	45.9			5	23.6	24.8	-3	13	2	73.5	72.3			7	86.7	71.6			9	92.3	79.0
-9	13	2	22.9	20.2	-5	6	1	90.7	83.7			8	93.4	96.7			10	195.0	194.7	2	3	2	10.4	9.5
		5	33.2	32.2			4	201.0	216.1	-3	14	4	20.9	23.7	0	3	3	113.3	111.7			5	113.9	110.1
		8	35.6	33.2			7	96.0	89.1			7	16.4	17.3			6	144.2	142.7			8	33.2	26.6
-9	14	1	11.7	12.7			10	15.2	19.7			10	100.6	106.4			9	40.4	32.1	2	4	1	16.2	21.2
		4	70.0	68.9	-5	7	3	2.2	1.2	-3	15	3	32.7	36.6	0	4	2	149.6	160.5			4	156.1	165.6
		7	17.4	16.8			6	119.1	114.2			6	36.5	33.9			5	2.1	2.9			7	55.8	54.5
		10	69.4	70.2			9	12.3	11.5			9	37.3	42.1			8	146.3	147.4			10	39.2	41.1
-9	15	3	43.1	45.3	-5	8	2	14.0	11.2	-2	3	1	125.3	117.9	0	5	1	70.0	57.0	2	5	0	142.1	135.5
		6	84.3	87.7			5	69.0	60.5			4	91.7	82.0			4	155.6	170.1			3	54.6	45.2
		9	64.2	68.9			8	30.6	27.2			7	17.8	16.4			7	30.3	19.0			6	120.6	123.3
-9	16	5	19.9	23.9	-5	9	1	50.8	46.3			10	216.9	219.2			10	57.5	54.2			9	16.2	12.1
		8	22.8	25.4			4	149.2	154.2	-2	4	3	81.9	61.4	0	6	3	65.5	52.3	2	6	2	16.8	15.3
-8	9	1	99.9	91.0			7	2.4	7.7			6	180.3	187.1			6	53.5	46.3			5	115.6	116.7
		4	117.1	117.0			10	97.0	90.5			9	127.7	120.7			9	30.8	25.5			8	45.4	41.1
		7	101.3	94.3	-5	10	3	52.3	44.6	-2	5	2	10.5	11.2	0	7	2	126.9	130.6	2	7	1	21.5	20.4
		10	83.6	77.8			6	138.3	139.2			5	97.3	88.7			5	18.6	10.4			4	160.4	170.4
-8	10	3	52.7	46.2			9	24.4	21.2			8	37.1	27.4			8	158.0	170.0			7	24.5	20.3
		6	91.9	90.0	-5	11	2	2.5	6.7	-2	6	1	66.1	60.9	0	8	1	2.4	4.1			10	109.0	109.2
		9	28.4	25.7			5	41.1	37.7			4	135.7	139.8			4	100.2	99.1	2	8	0	85.7	84.0
-8	11	2	39.2	35.2			8	16.1	17.5			7	130.2	134.4			7	2.8	0.9			3	44.6	40.4
		5	2.7	6.1	-5	12	1	28.2	25.7			10	147.0	138.4			10	136.1	141.2			6	93.3	92.6
		8	63.0	60.3			4	83.6	85.0	-2	7	3	96.0	82.5	0	9	3	15.3	11.3			9	73.6	70.4
-8	12	1	70.8	65.3			7	21.4	21.1			6	129.0	129.1			6	107.1	106.1	2	9	2	26.3	22.3
		4	119.7	122.3			10	87.3	88.1			9	75.5	66.8			9	12.7	12.4			5	89.0	87.1
					-5	13	3	52.7	50.4	-2	8	2	15.3	15.7	0	10	2	113.9	112.0			8	13.2	11.5
		7	85.2	83.4			6	86.8	86.6			5	92.6	89.7			5	2.7	2.1	2	10	1	16.8	13.0
		10	34.9	36.1			9	59.8	59.8			8	33.6	30.7			8	101.7	102.7			4	91.7	93.1
-8	13	3	66.5	64.3	-5	14	2	2.9	5.2	-2	9	1	50.3	43.8	0	11	1	19.8	16.7			7	29.3	19.6
		6	99.5	100.5			5	34.8	35.5			4	111.2	110.6			4	15.5	21.3			10	59.9	62.0
		9	34.8	34.6			8	2.9	8.1			7	19.6	14.8			7	2.8	7.0	2	11	0	56.8	57.3
-8	14	2	39.4	39.9	-5	15	1	18.8	17.2			10	61.3	62.6			10	123.1	128.5			3	35.7	35.8
		8	60.2	63.0			4	75.9	78.5	-2	10	3	66.0	58.0	0	12	3	21.5	18.3			6	77.8	77.4
-8	15	1	18.2	18.2			7	19.2	20.1			6	72.3	74.5			6	81.1	81.0			9	45.0	44.6
		4	80.6	84.9			10	23.9	20.0			9	51.2	43.6			9	14.4	13.2	2	12	2	2.9	5.2
		7	33.1	32.7	-4	5	3	105.4	94.2	-2	11	2	15.8	14.2	0	13	2	29.1	27.4			5	11.6	9.0
		10	69.0	70.7			6	118.2	110.4			5	66.0	62.4			8	38.7	36.5			8	16.9	17.3
-8	16	3	41.6	45.7			9	86.5	74.2			8	16.6	19.1	0	14	7	11.5	14.6	2	13	1	37.8	42.5
		6	66.2	70.5	-4	6	2	16.9	12.0	-2	12	1	28.2	27.7	1	0	1	19.1	14.2			4	62.9	69.5
		9	31.2	37.3			5	127.1	120.2			4	115.1	110.1			4	166.0	180.1	3	0	0	174.1	197.5
-7	8	3	27.1	20.1			8	33.9	29.1			7	51.2	49.5			7	18.8	12.8			3	142.7	137.9
		6	33.5	31.4	-4	7	1	2.7	4.0			10	68.9	67.3			10	74.6	69.0			6	99.8	98.9
		9	43.1	37.2			4	104.0	87.1	-2	13	3	48.2	47.8	1	1	0	117.0	133.9			9	78.6	63.6
-7	9	2	22.5	16.3			7	70.1	58.5			6	71.3	72.2			3	179.0	191.0	3	1	2	117.1	110.6
		5	19.3	17.7			10	196.6	203.9			9	2.9	8.6			6	198.0	207.2			5	57.0	47.0
		8	27.7	26.1	-4	8	3	51.2	44.3	-2	14	2	2.9	5.8			9	152.8	148.2			8	161.7	159.4

Table 5. *(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	$\|F_o\|$	$\|F_c\|$
3	2	1	117.5	111.3	4	7	0	183.1	193.7	6	2	4	184.4	192.8	7	9	7	15.4	11.6	10	1	0	108.1	110.4
		4	180.0	190.5			3	26.6	22.6			7	123.3	118.7	8	0	2	70.5	62.9			3	22.9	19.2
		7	124.5	117.1			6	2.9	14.7			10	93.7	86.0			5	2.4	1.9			6	58.9	58.9
		10	116.4	100.5			9	9.7	9.2	6	3	0	126.1	123.4			8	99.4	91.9			9	22.5	18.4
3	3	0	206.8	235.7	4	8	2	2.7	5.8			3	28.3	24.6	8	1	1	56.8	56.9	10	2	2	28.8	30.8
		3	128.5	118.2			5	40.3	36.5			6	86.6	82.1			4	164.7	167.1			5	32.9	31.8
		6	19.2	19.7			8	14.5	12.0			9	39.9	35.3			7	39.2	40.1			8	13.7	14.0
		9	32.5	25.2	4	9	1	21.8	20.6	6	4	2	63.4	59.3			10	20.9	26.7	10	3	1	2.8	5.1
3	4	2	136.0	138.3			4	68.1	69.3			5	2.4	7.8	8	2	0	138.9	137.3			7	30.3	29.5
		5	24.4	20.7			7	29.0	27.5			8	82.6	80.6			3	14.2	15.3			10	129.9	138.5
		8	150.1	156.3			10	80.5	85.7	6	5	1	36.2	34.3			6	70.8	78.1	10	4	0	122.3	129.8
3	5	1	82.0	74.2	4	10	0	111.6	115.8			4	120.1	120.5			9	17.5	20.9			3	2.9	6.7
		4	131.9	133.3			3	2.9	2.7			7	12.2	15.4	8	3	2	59.8	56.6			6	2.6	14.2
		7	87.1	80.8			6	39.0	40.5			10	66.8	67.0			5	40.4	36.0			9	2.9	2.6
		10	108.5	105.5			9	17.4	18.0	6	6	0	55.1	55.8			8	75.6	72.0	10	5	2	13.8	16.6
3	6	0	91.0	89.8	4	11	2	50.0	54.3			3	88.7	84.9	8	4	1	39.8	38.4			5	20.6	18.5
		3	11.4	13.2			5	21.4	20.2			6	113.8	115.3			4	103.3	103.0			8	2.9	7.2
		6	135.9	138.3			8	47.6	47.9			9	50.1	57.1			7	76.8	73.3	10	6	1	23.4	25.5
		9	2.4	10.9	5	0	2	41.5	32.0	6	7	2	23.0	19.5			10	76.3	77.4			4	48.8	50.5
3	7	2	129.1	129.5			5	13.7	2.5			5	2.8	2.4	8	5	0	34.8	36.8			7	18.4	21.9
		5	2.7	2.0			8	16.7	11.0			8	53.1	50.2			3	52.0	50.9	11	0	2	75.5	74.0
		8	130.7	135.1	5	1	1	140.8	146.5	6	8	1	13.2	12.3			6	110.3	112.0			5	2.8	2.0
3	8	1	57.5	40.2			4	197.7	208.8			4	42.9	43.7			9	85.3	85.2			8	83.4	80.1
		4	70.8	68.1			7	193.4	194.7			7	26.7	29.5	8	6	2	55.9	55.0	11	1	1	57.0	54.9
		7	38.2	34.0			10	117.5	105.1			10	96.8	100.4			5	16.7	12.3			4	72.5	71.1
		10	72.7	75.6	5	2	0	72.2	68.3	6	9	0	40.6	41.5			8	60.5	60.9			7	42.6	39.2
3	9	0	70.7	70.1			3	29.8	65.1			3	31.8	30.6	8	7	1	18.0	12.9			10	79.1	79.3
		3	70.0	68.5			6	177.2	179.3			6	66.1	66.3			4	56.6	57.2	11	2	0	57.0	55.0
		6	69.0	69.8			9	12.9	4.9			9	29.0	32.1			7	2.9	4.7			3	48.0	48.1
		9	27.8	26.5	5	3	2	31.1	25.2	6	10	2	14.9	14.1			10	59.6	59.8			6	54.0	51.3
3	10	2	66.3	66.0			5	67.9	61.0			5	16.6	16.7	8	8	0	40.6	42.7			9	29.4	29.4
		5	16.2	16.2			8	31.7	28.8	7	0	1	15.5	14.4			3	46.7	51.1	11	3	2	52.0	49.9
		8	81.1	83.1	5	4	1	117.7	112.7			4	15.6	23.8			6	51.8	53.5			5	25.7	24.3
3	11	1	2.9	2.3			4	115.1	114.9			7	19.3	16.1			9	62.7	72.1			8	77.3	79.5
		4	46.3	46.0			7	64.3	60.7			10	217.6	229.3	9	0	0	100.6	98.0	11	4	1	23.2	25.1
		7	2.9	7.8			10	95.2	91.7	7	1	0	133.4	132.1			3	21.6	19.7			4	61.9	64.2
		10	102.4	111.7	5	5	0	96.5	95.5			3	2.4	4.0			6	110.9	107.5			7	22.7	21.3
3	12	0	38.1	37.1			3	102.7	95.2			6	111.5	106.0			9	30.8	28.3			10	56.3	53.1
		3	21.4	21.0			6	104.6	104.0			6	111.5	104.9	9	1	2	37.7	34.5	11	5	0	55.6	61.4
		6	74.3	83.3			9	76.6	70.5			9	16.8	12.7			5	52.3	45.4	12	0	0	55.7	55.7
		9	3.0	8.4	5	6	2	20.8	19.8	7	2	2	10.0	10.8			8	18.0	17.3			3	2.9	1.2
4	0	1	56.1	42.6			5	41.6	40.4			5	23.9	18.3	9	2	1	70.7	66.7			6	77.1	77.7
		4	42.7	37.3			8	14.2	16.3			8	40.2	36.0			4	92.0	91.9			9	24.8	26.1
		7	1.9	1.2	5	7	1	2.5	6.3	7	3	1	2.5	6.2			7	69.5	65.8	12	1	2	2.9	9.0
		10	210.0	222.7			4	94.9	98.0			4	34.6	34.5			10	51.2	51.5			5	39.9	39.1
4	1	0	145.6	146.6			7	2.7	2.6			7	12.2	7.8	9	3	0	35.7	37.5			8	15.3	19.6
		3	118.1	100.2			10	61.1	61.1			10	144.9	152.9			3	44.9	40.2	12	2	1	2.9	7.1
		6	187.3	190.4	5	8	0	45.3	45.9	7	4	0	155.4	160.6			6	85.5	84.4			4	85.8	90.6
		9	121.6	112.3			3	42.9	42.1			3	26.9	22.4			9	22.8	20.6			7	13.9	15.7
4	2	2	38.1	32.0			6	90.6	93.0			6	2.6	15.3	9	4	2	25.6	22.4			10	55.0	58.4
		5	92.2	81.5			9	41.7	40.0			9	43.1	35.7			5	35.4	35.6	12	3	0	55.6	55.9
		8	56.0	47.5	5	9	2	13.7	11.5	7	5	2	2.7	5.9			8	48.1	47.1			3	27.2	27.9
4	3	1	33.4	25.3			5	14.1	12.9			5	17.1	16.7	9	5	1	39.6	36.6			6	62.1	61.8
		4	41.5	38.2			8	22.3	21.7			8	33.5	33.3			4	95.9	98.2			9	3.0	4.9
		7	10.9	6.1	5	10	1	16.8	20.5	7	6	1	2.8	5.7			7	35.3	36.1	13	0	1	33.0	33.0
		10	229.2	244.2			4	72.5	75.3			4	57.0	57.1			10	32.2	29.6			4	52.4	50.2
4	4	0	129.5	129.3			7	11.4	14.9			7	2.8	1.0	9	6	0	69.5	73.6			7	26.5	27.7
		3	61.6	53.2			10	47.1	46.8			10	120.9	126.0			3	41.8	42.3			10	63.2	61.8
		6	49.8	45.8	5	11	0	50.3	55.1	7	7	0	119.7	126.4			6	79.3	82.9	13	1	0	85.1	90.1
		9	54.4	49.2	6	0	0	183.6	196.6			3	23.1	23.3			9	41.4	45.7			3	13.2	11.8
4	5	2	13.1	8.7			3	12.1	5.4			6	15.1	19.4	9	7	2	13.7	14.9			6	44.1	45.1
		5	79.1	72.7			6	105.2	92.2			9	10.8	7.3			5	3.2	12.7			9	3.0	4.4
		8	9.0	14.6			9	60.4	49.9	7	8	2	2.9	3.0			8	18.0	16.4	14	0	2	78.3	88.0
4	6	1	2.5	5.6	6	1	2	71.3	62.2			5	22.2	21.7	10	0	1	18.4	18.1			5	3.0	2.4
		4	47.2	46.6			5	21.8	18.9			8	27.3	26.4			4	17.1	24.3					
		7	11.2	4.8			8	106.6	96.0	7	9	1	3.0	8.2			7	40.9	34.7					
		10	119.7	125.1	6	2	1	99.0	92.3			4	55.6	60.2			10	151.2	154.1					

$|F_c|$ values, obtained with the parameters in Tables 2 and 4 is made in Table 5. Owing to the large number of the measured reflections, only the first 834 (up to $l = 10$) are included in the table. The rest are available on request. Interatomic distances and bond angles are given in Tables 6 and 7, in which the indices in parentheses refer to the atoms in Figs. 2 und 3.

Description of the structure and discussion

The two Fe atoms of the asymmetric unit occupy the special position $6c$ on the threefold axis, wheras all the other atoms occupy the general position $18f$. Figure 1 is a clinographic projection of the rhombohedral unit cell. In the asymmetric unit of the cell there is one

Table 6. *Interatomic distances in rhombohedral* $Fe_2(SO_4)_3$ *with their standard deviations*

	SO_4 tetrahedron		
S—O(1)	1.465 Å	O(1)—O(2)	2.408 Å
O(2)	1.468	O(3)	2.396
O(3)	1.463	O(4)	2.364
O(4)	1.465	O(2)—O(3)	2.370
Average S—O	1.465(2)	O(4)	2.420
		O(3)—O(4)	2.400
		Average O—O	2.393(3)
	$Fe(1)O_6$ octahedron		
Fe(1)—O(1)	1.980 Å	O(1)—O′(1)	2.849 Å
O′(1)	1.980	O″(1)	2.849
O″(1)	1.980	O′(3)	2.963
O′(3)	1.983	O″(3)	2.674
O″(3)	1.983	O′(1)—O″(1)	2.849
O‴(3)	1.983	O″(3)	2.963
Average Fe(1)—O	1.981(2)	O‴(3)	2.674
		O′(3)—O″(1)	2.674
		O″(3)	2.728
		O‴(3)	2.728
		O‴(3)—O″(1)	2.963
		O″(3)	2.728
		Average O—O	2.803(3)
	$Fe(2)O_6$ octahedron		
Fe(2)—O(2)	1.993 Å	O(2)—O′(2)	2.808 Å
O′(2)	1.993	O″(2)	2.808
O″(2)	1.993	O′(4)	2.791
O′(4)	1.984	O‴(4)	2.800
O″(4)	1.984	O′(2)—O″(2)	2.808
O‴(4)	1.984	O′(4)	2.800
Average Fe(2)—O	1.988(2)	O″(4)	2.791
		O″(4)—O″(2)	2.800
		O′(4)	2.848
		O‴(4)	2.848
		O‴(4)—O″(2)	2.791
		O′(4)	2.848
		Average O—O	2.812(2)

SO_4 tetrahedron and two different FeO_6 octahedra. As in the case of monoclinic $Fe_2(SO_4)_3$ (CHRISTIDIS and RENTZEPERIS, 1975) all the coordination polyhedra are isolated. The SO_4 tetrahedron shares each of its vertices with an FeO_6 octahedron and each FeO_6 octahedron is

Table 7. *Bond angles in rhombohedral* $Fe_2(SO_4)_3$ *with their standard deviations*

SO_4 tetrahedron

O(1)—S—O(2)	110.34°
O(3)	109.79
O(4)	107.56
O(2)—S—O(3)	107.89
O(4)	111.17
O(3)—S—O(4)	110.09
Average	109.47(14)

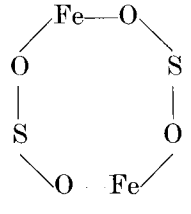
$Fe(1)O_6$ octahedron

O(1)—Fe(1)—O′(1)	92.00°
O″(1)	92.00
O′(3)	96.75
O″(3)	84.86
O′(1)—Fe(1)—O″(1)	92.00
O″(3)	96.75
O‴(3)	84.86
O′(3)—Fe(1)—O″(1)	84.86
O″(3)	86.91
O‴(3)	86.91
O‴(3)—Fe(1)—O″(1)	96.75
O″(3)	86.91
Average	90.13(9)

$Fe(2)O_6$ octahedron

O(2)—Fe(2)—O′(2)	89.57°
O″(2)	89.57
O′(4)	89.16
O‴(4)	89.52
O′(2)—Fe(2)—O″(2)	89.57
O′(4)	89.52
O″(4)	89.16
O″(4)—Fe(2)—O″(2)	89.52
O′(4)	91.73
O‴(4)	91.73
O‴(4)—Fe(2)—O″(2)	89.16
O′(4)	91.73
Average	89.99(9)

linked to six SO_4 tetrahedra. Thus a three-dimensional network of tetrahedra and octahedra is formed, in which each O atom is bonded to only one S and one Fe atom. As can be seen in Fig. 2, which is a projection of the hexagonal unit cell on the $(11\bar{2}0)$ plane, the eight-membered non-planar rings of the form already met in the structure of monoclinic $Fe_2(SO_4)_3$, are also present



in the rhombohedral structure. In Fig. 3 are shown the coordination polyhedra around the cations with the corresponding interatomic

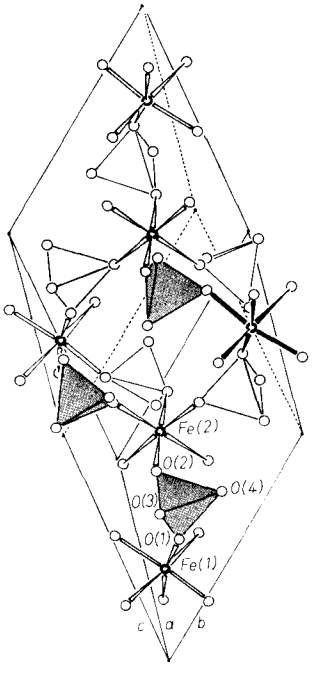


Fig. 1

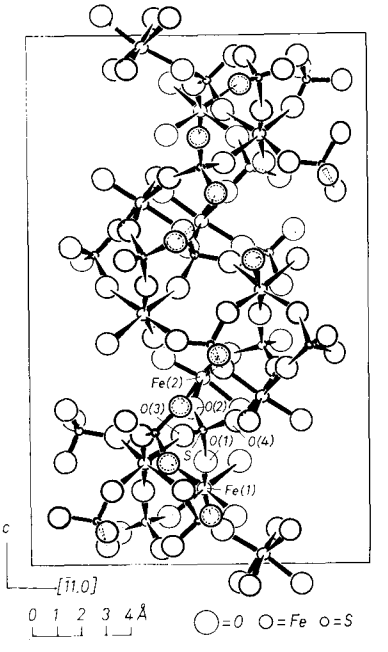


Fig. 2

Fig. 1. Clinographic projection of the rhombohedral unit cell of $Fe_2(SO_4)_3$. Tetrahedra SO_4, at various heights in x, are differently shaded

Fig. 2. Normal projection of the hexagonal unit cell of rhombohedral $Fe_2(SO_4)_3$ on the $(11\bar{2}0)$ plane. Atoms with greater heights from the plane of projection are indicated with heavier circles. In case of atoms differing by a whole translation the lower atom is shown as a dashed circle

distances. The SO_4 tetrahedron is almost regular with virtually equal S—O distances, averaging to 1.465 Å. The average O—O distance is 2.393 Å. The tetrahedral bond angles are very near the ideal value 109.46°, with deviations not exceeding 1.9°. These values almost coincide with those of the three SO_4 tetrahedra in the monoclinic $Fe_2(SO_4)_3$.

The two FeO_6 octahedra are only slightly distorted. In each, the Fe—O distances are almost equal, averaging to 1.981 Å and 1.988 Å respectively. The corresponding average O—O distances are 2.803 Å and 2.812 Å. The bond angles differ from 90° by less than 5°. Both FeO_6 octahedra are similar to those found in monoclinic $Fe_2(SO_4)_3$,

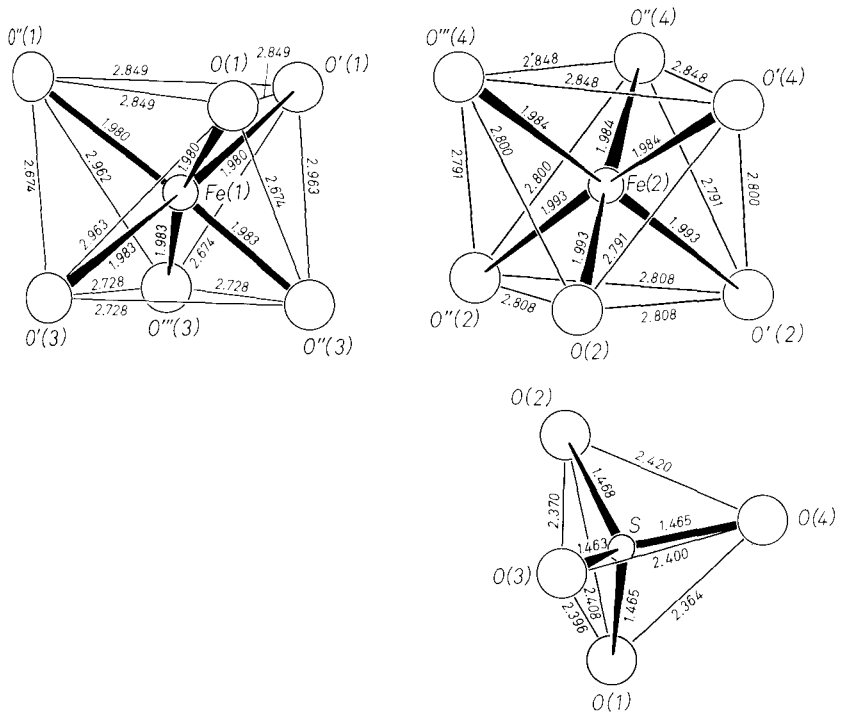


Fig. 3. Clinographic projections of the coordination polyhedra around the cations. The orientations of the polyhedra are for the cations shown in Fig. 1

although the latter are a little bit more distorted. The comparison with the FeO_6 octahedra in other structures, made in our paper on the monoclinic $Fe_2(SO_4)_3$ (CHRISTIDIS and RENTZEPERIS, 1975) holds also for the rhombohedral modification. Actually, the monoclinic structure may be regarded as a slightly distorted form of the rhombohedral. This easily explains the fact that, under slightly different conditions of preparation, the one or the other, or both modifications together, are obtained.

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Note added in proof: When this paper was in proof and ready for publication our attention was drawn to an earlier work on the same subject, which had escaped our notice. We gladly cite this paper: R. MASSE, J.-C. GUITEL et R. PERRET (1973), Structure cristalline de la varieté rhomboédrique du sulfate ferrique $Fe_2(SO_4)_3$. Bull. Soc. franç. Min. Cristallogr. **96**, 346—349.

Literature

P. C. CHRISTIDIS and P. J. RENTZEPERIS (1975), The crystal structure of the monoclinic $Fe_2(SO_4)_3$. Z. Kristallogr. **141**, 233—245.

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.

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

R. W. JAMES and G. W. BRINDLEY (1931), Some numerical values of the atomic scattering factor. Z. Kristallogr. **78**, 470—478.

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. Munksgaard, Copenhagen, pp. 291—294.

KATHLEEN LONSDALE (1968), *International tables for x-ray crystallography,* 2nd edit., vol. III, pp. 204—205 and 215.

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.