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The crystal structure of amarantite, $Fe_2(SO_4)_2O \cdot 7H_2O$

By P. SÜSSE

Crystallographic Laboratory, Massachusetts Institute of Technology
Cambridge, Massachusetts

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Auszug

Amarantit ist triklin, Raumgruppe $P\bar{1}$. Die Gitterkonstanten sind $a = 8{,}976$ Å, $b = 11{,}678$ Å, $c = 6{,}698$ Å, $\alpha = 95{,}65°$, $\beta = 90{,}36°$, $\gamma = 97{,}20°$. Die Elementarzelle enthält zwei Formeleinheiten. Die Reflex-Intensitäten wurden mit einem Einkristallgoniometer gemessen. Außer der Korrektur mit dem Polarisations- und Lorentzfaktor wurde eine genaue Absorptionskorrektur durchgeführt. Die Kristallstruktur wurde mit Hilfe von dreidimensionalen Patterson- und Fouriersynthesen bestimmt. Alle Atome besetzen die allgemeine Punktlage $2i$. Die Parameter wurden nach der Methode der Kleinsten Quadrate verfeinert. Der R-Wert für alle Reflexe ist 5,2%. Eine abschließende dreidimensionale Differenz-Fouriersynthese führte zur Bestimmung wahrscheinlicher Wasserstoffpositionen.

Die Struktur besteht aus Fe-Koordinationsoktaedern und Sulfat-Tetraedern, die zu Ketten parallel zur c-Achse verknüpft sind. Untereinander werden die einzelnen Ketten nur durch Wasserstoffbrücken-Bindungen zusammengehalten. Drei Wassermoleküle befinden sich zwischen den Ketten und sind nicht an Kationen gebunden. Die bisherige chemische Formel des Amarantits, $2(FeSO_4OH \cdot 3H_2O)$, steht nicht im Einklang mit dem Ergebnis dieser Untersuchung, die vielmehr zu der Formel $Fe_2(SO_4)_2O \cdot 7H_2O$ führt.

Abstract

Amarantite is triclinic, space group $P\bar{1}$. The lattice constants are $a = 8.976$ Å, $b = 11.678$ Å, $c = 6.698$ Å, $\alpha = 95.65°$, $\beta = 90.36°$, $\gamma = 97.20°$. The unit cell contains two formula units. The reflection intensities were measured with a single-crystal diffractometer and accurately corrected for absorption. The determination of the crystal structure was carried out with the aid of three-dimensional Patterson and Fourier syntheses. All atoms occupy the general position $2i$. The parameters were refined by the full-matrix least-squares method yielding an R value for all reflections of 5.2%. The positions of the hydrogen atoms of the water molecules have been determined by means of a final three-dimensional difference-Fourier synthesis.

The structure consists of Fe coordination octahedra and sulfate tetrahedra connected to form chains parallel to the c axis, linked to each other only by hydrogen bonds. Three water molecules are located between the chains and are not connected with cations. According to the results of this investigation the chemical formula of amarantite is not $2(FeSO_4OH \cdot 3H_2O)$ but $Fe_2(SO_4)_2O \cdot 7H_2O$.

Introduction

Amarantite occurs in deposits of desert areas associated with other sulfate minerals. While these sulfate minerals have been studied optically and chemically[1,2], only a few of their crystal structures are known[3,4]. The determination of the crystal structure of amarantite, including its hydrogen bond system, is reported in this paper.

Experimental

Amarantite is triclinic, space group $P\bar{1}$. The crystals studied in this investigation were from Quetena, Chile and were kindly supplied by Professor J. ZEMANN of the University of Vienna.

The lattice constants, which had already been measured by CESBRON[5], were refined from powder diffractometer data by the method of least squares. The resulting cell constants are seen in Table 1.

Table 1. *Crystallographic data for amarantite from Quentena*

$a = 8.976 \pm .001$ Å	$\alpha = 95.65 \pm .02°$
$b = 11.678 \pm .002$ Å	$\beta = 90.36 \pm .01°$
$c = 6.698 \pm .002$ Å	$\gamma = 97.20 \pm .02°$

$a:b:c$	$= 0.7686:1:0.5735$
volume	$= 693.1$ Å^3
ϱ_{obs}	$= 2.20$ gcm^{-3}
ϱ_{calc}	$= 2.14$ gcm^{-3}
Z	$= 2[Fe_2(SO_4)_2O \cdot 7H_2O]$
space group	$= P\bar{1}$

[1] R. SCHARITZER, Beiträge zur Kenntnis der chemischen Konstitution und der Genese der natürlichen Ferrisulfate. Z. Kristallogr. **65** (1927) 335—360.

[2] M. C. BANDY, Mineralogy of three sulphate deposits of Northern Chile. Amer. Mineral. **23** (1938) 669—760.

[3] E. J. GRAEBER, B. MOROSIN and A. ROSENZWEIG, The crystal structure of krausite, $KFe(SO_4)H_2O$. Amer. Mineral. **50** (1965) 1929—1936.

[4] P. SÜSSE, Die Kristallstruktur des Botryogens. Naturwiss. **54** (1967) 139.

[5] F. CESBRON, Contributions à la minéralogie des sulfates de fer hydratés. Bull. Soc. franç. Minér. Cristallogr. **87** (1964) 125—143.

A prismatic crystal with the dimensions $0.10 \times 0.14 \times 0.26$ mm was selected for use in measuring intensities. This was carried out be means of a single-crystal diffractometer based on Weissenberg geometry. The crystal was rotated about the c axis, and the diffracted Fe$K\alpha$ radiation was measured with a proportional counter. Within the range of the diffractometer, 1141 reflections were explored, of which 199 had intensities below the detectable limit. These 199 reflections were assigned an arbitrary intensity of half of the value of the smallest measurable reflection. The intensities were corrected for Lorentz and polarization factors and for absorption.

The determination of the structure

The positions of the two iron and the two sulfur atoms were determined with the aid of a three-dimensional Patterson synthesis. Two cycles of structure-factor calculations and Fourier syntheses led to the determination of the positions of all 20 independent nonhydrogen atoms. These were all found to occupy the general position $2i$. At this stage, with an overall temperature coefficient of $B = 1.0$ Å^2 the R value was 15%.

The refinement of the parameters

The refinement was carried out by means of the full-matrix least-squares method. All reflections were given unit weights, but only 918 of the 1141 were used in course of the refinement, the 199 observed as having zero intensity and the 24 strongest reflections being omitted. Three scale factors were used. The atomic-scattering curves of Fe^{3+}, S, $O^{-1/2}$ (for the sulfate oxygen atoms), O^{-1} (for the rest of the oxygen atoms), and H, were prepared from the values given in the *International tables*[6]. The scattering by the hydrogen atoms was neglected during the least-squares refinement.

In the first stage, the scale factors, the positional parameters, and the isotropic temperature coefficients of the 20 independent atoms were refined. This stage ended with an R value of 5.7%. In the next stage only the anisotropic temperature coefficients were varied and refined, reducing R to 3.9%. In a final run the positional parameters were varied again, but this resulted in no significant changes in the atom positions or the R value. In the final structure-factor calculation

[6] International tables for x-ray crystallography, vol. III. The Kynoch Press, Birmingham (1962) 202—205.

Table 2. *Observed and calculated structure factors*

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
0	0	0		464.0	-3	7	0	52.6	52.3	5	7	1	16.9	- 17.3	-1	9	1	21.9	- 20.1
	1		72.8	87.8		8		4.0	2.9	6	0	1	11.0	10.7		10		33.6	- 32.6
	2		34.5	- 32.4		9		19.5	- 19.1		1		23.8	- 22.4	-2	0	1	83.6	- 90.7
	3		61.4	58.8		10		23.9	- 23.3		2		72.6	- 75.3		1		23.6	24.0
	4		8.6	9.2	-4	1	0	59.3	- 60.3		3		36.4	- 36.1		2		50.7	49.9
	5		42.3	37.0		2		8.6	13.4		4		48.4	- 47.6		3		22.5	24.4
	6		94.2	- 95.3		3		50.8	54.7		5		1.6	- 2.8		4		22.6	- 16.7
	7		98.6	-101.5		4		41.4	40.2		6		15.3	21.0		5		107.9	-106.5
	8		8.2	6.5		5		1.8	- 1.2	7	0	1	24.9	24.7		6		21.1	22.4
	9		6.1	- 6.2		6		4.6	- 1.4		1		3.8	- 3.2		7		48.5	48.9
	10		54.2	- 53.8		7		42.4	42.6		2		1.6	- 0.2		8		35.3	- 34.8
1	0	0	92.4	136.7		8		33.6	31.8		3		8.0	- 6.2		9		37.8	- 38.2
	1		31.4	31.4		9		33.3	- 33.4		4		38.1	- 42.3		10		15.1	- 14.0
	2		44.8	42.2		10		36.7	- 35.2	8	0	1	18.3	- 17.5	-3	0	1	9.4	- 1.1
	3		21.1	16.6	-5	1	0	35.5	- 37.4		1		6.6	8.9		1		3.8	- 6.7
	4		44.2	- 39.3		2		14.9	13.3	0	-1	1	21.1	- 14.7		2		1.5	3.8
	5		35.4	- 31.1		3		9.6	11.9		-2		28.2	- 25.0		3		21.4	- 17.8
	6		60.3	- 59.3		4		16.5	- 15.2		-3		77.3	- 78.4		4		4.8	2.6
	7		62.3	- 61.4		5		18.0	- 16.0		-4		73.6	- 72.8		5		23.5	- 20.7
	8		1.0	0.0		6		40.9	40.3		-5		3.3	- 3.3		6		12.6	14.7
	9		4.6	- 2.5		7		23.1	21.8		-6		32.3	- 30.8		7		49.3	50.1
	10		41.0	- 40.4		8		4.9	- 4.2		-7		67.0	- 68.7		8		7.9	8.4
2	0	0	26.9	- 24.1		9		9.4	- 9.0		-8		4.8	- 7.2		9		0.6	3.4
	1		8.3	12.4	-6	1	0	55.0	- 55.9		-9		48.1	48.1		10		13.2	12.6
	2		20.5	- 22.8		2		20.2	- 19.7		-10		7.6	7.4	-4	0	1	5.1	- 3.8
	3		65.0	- 71.0		3		15.1	15.0	1	-1	1	72.8	82.0		1		63.1	- 65.7
	4		30.7	- 30.6		4		41.9	- 41.5		-2		42.3	- 42.5		2		17.6	- 13.1
	5		30.0	- 27.3		5		41.0	- 40.7		-3		37.8	36.2		3		5.7	5.0
	6		45.1	- 46.8		6		31.8	31.0		-4		14.6	13.9		4		43.5	- 45.6
	7		46.8	- 47.0		7		12.5	10.5		-5		2.2	3.0		5		37.8	36.2
	8		5.4	6.5		8		10.3	- 10.4		-6		31.3	25.6		6		41.3	41.5
	9		23.7	22.9	-7	1	0	16.7	- 16.8		-7		55.2	- 56.7		7		34.7	35.1
	10		18.7	18.8		2		21.5	- 23.0		-8		23.2	- 22.2		8		50.2	52.3
3	0	0	48.5	- 45.7		3		3.7	3.2		-9		36.6	35.3		9		19.5	19.9
	1		13.0	- 13.0		4		39.9	- 39.7		-10		29.1	- 28.7	-5	0	1	34.8	- 35.8
	2		2.6	- 3.5		5		3.9	- 4.1	2	-1	1	104.3	121.2		1		67.6	- 66.3
	3		28.0	- 34.6		6		48.3	47.6		-2		4.0	5.8		2		34.9	- 33.1
	4		39.5	- 38.6		7		22.5	21.1		-3		48.5	46.8		3		21.6	- 23.3
	5		24.2	- 23.3	-8	1	0	5.4	5.8		-4		7.1	15.4		4		57.5	- 58.5
	6		13.9	- 13.8		2		3.8	- 3.0		-5		11.7	- 8.8		5		31.6	31.0
	7		6.6	- 7.3		3		10.5	10.8		-6		2.9	- 1.3		6		44.9	45.0
	8		8.7	- 0.4		4		5.1	- 4.2		-7		67.2	- 68.5		7		12.5	11.0
	9		22.5	21.6	0	0	1		40.4		-8		73.1	- 74.0		8		44.2	44.6
4	0	0	15.4	- 16.5		1		40.1	- 39.9		-9		21.9	- 23.4		9		38.7	39.8
	1		55.2	53.6		2		6.6	- 7.7		-10		41.1	- 42.1	-6	0	1	13.3	- 11.2
	2		47.0	- 46.7		3		131.1	143.7	3	-1	1	46.4	50.5		1		23.7	23.9
	3		86.0	- 90.7		4		51.1	50.9		-2		16.7	16.4		2		7.3	7.3
	4		42.2	- 42.5		5		6.8	- 10.4		-3		39.1	37.2		3		35.0	- 34.8
	5		5.9	- 5.8		6		27.3	26.0		-4		28.7	34.0		4		55.5	- 55.4
	6		20.8	20.6		7		9.4	9.0		-5		15.7	15.5		5		5.6	5.4
	7		31.9	- 32.4		8		12.2	12.2		-6		57.2	- 59.2		6		46.8	47.2
	8		34.8	- 36.2		9		9.3	10.7		-7		43.9	- 44.2		7		4.2	- 4.9
5	0	0	38.6	- 39.9		10		30.7	- 28.0		-8		41.9	- 43.6		8		23.9	- 24.5
	1		32.1	28.6	1	0	1	71.5	76.0		-9		39.4	- 39.0	-7	0	1	24.7	24.4
	2		4.1	- 5.3		1		49.6	- 49.7		-10		3.0	- 0.9		1		39.6	39.6
	3		10.0	- 9.0		2		17.6	- 19.0	4	-1	1	6.4	5.6		2		29.5	- 29.1
	4		26.1	- 25.8		3		16.9	- 12.5		-2		2.2	2.8		3		39.1	- 38.0
	5		20.6	- 19.6		4		1.3	1.8		-3		66.1	67.2		4		36.1	- 34.3
	6		40.8	40.0		5		3.9	0.8		-4		80.9	85.7		5		24.3	- 24.7
	7		14.2	- 14.7		6		41.5	- 41.6		-5		24.5	24.2		6		2.1	- 0.9
6	0	0	24.3	- 25.1		7		41.8	- 41.2		-6		41.3	- 40.8	-8	0	1	3.4	- 7.2
	1		2.3	- 0.3		8		1.1	- 1.7		-7		13.1	12.5		1		11.9	10.4
	2		47.8	48.1		9		5.4	5.9		-8		42.7	43.3		2		42.7	- 41.6
	3		34.2	34.1		10		20.9	- 19.0		-9		9.9	- 8.7		3		52.9	- 52.7
	4		15.1	- 13.8	2	0	1	106.8	118.7		-10		3.5	4.8	-1	-1	1	8.6	- 8.1
	5		43.0	43.4		1		22.7	- 23.2	5	-1	1	39.1	- 39.6		-2		5.5	7.9
	6		54.1	53.6		2		55.7	52.9		-2		15.2	- 14.0		-3		109.3	-116.9
7	0	0	30.1	- 28.0		3		19.8	19.1		-3		46.8	48.1		-4		89.0	- 95.5
	1		74.0	- 74.9		4		27.9	- 22.2		-4		57.3	58.8		-5		21.6	- 21.0
	2		25.6	24.0		5		3.5	2.8		-5		6.7	- 5.7		-6		15.2	- 14.0
	3		26.2	24.9		6		67.5	- 69.2		-6		12.2	- 11.8		-7		54.1	- 54.4
	4		14.1	- 13.2		7		30.0	- 29.3		-7		25.7	25.1		-8		18.1	- 20.1
8	0	0	28.6	- 28.2		8		19.4	17.9		-8		58.6	59.6		-9		35.0	34.8
	1		24.6	- 24.4		9		34.9	- 34.8		-9		9.2	9.9		-10		35.4	34.8
-1	1	0	29.7	27.9	3	0	1	99.4	108.8	6	-1	1	36.0	- 37.0	-2	-1	1	61.6	61.5
	2		40.6	- 34.1		1		21.6	22.5		-2		2.2	- 1.8		-2		20.8	18.3
	3		42.9	39.5		2		34.5	32.8		-3		26.3	27.2		-3		67.7	- 71.0
	4		12.5	- 7.8		3		2.5	- 5.7		-4		16.8	17.5		-4		49.7	- 53.2
	5		18.0	- 18.5		4		7.6	- 7.5		-5		3.2	- 1.1		-5		26.1	- 24.0
	6		30.6	- 32.5		5		13.1	13.4		-6		7.5	7.5		-6		33.9	33.6
	7		26.8	- 27.4		6		63.6	- 67.6		-7		19.6	18.4		-7		1.1	- 1.2
	8		7.1	7.9		7		27.5	- 27.6		-8		25.0	23.6		-8		15.2	- 14.1
	9		5.0	4.9		8		5.9	5.1	7	-1	1	5.9	6.3		-9		13.1	14.1
	10		10.3	- 9.1		9		20.6	- 23.0		-2		5.0	4.5		-10		42.8	41.6
-2	1	0	6.0	7.9	4	0	1	34.8	33.8		-3		22.5	21.8	-3	-1	1	62.1	59.2
	2		66.3	- 66.9		1		28.5	27.5		-4		7.6	6.8		-2		21.8	20.5
	3		15.0	18.3		2		42.7	- 44.1		-5		6.9	- 6.6		-3		19.7	- 21.0
	4		80.6	83.9		3		59.4	- 59.4		-6		14.4	13.9		-4		18.3	- 21.4
	5		28.4	- 26.4		4		19.7	18.6	8	-1	1	3.6	2.5		-5		2.6	- 2.6
	6		4.8	4.2		5		18.1	- 16.3		-2		24.0	- 23.6		-6		18.3	19.7
	7		34.9	34.0		6		46.6	- 47.5		-3		3.7	- 7.5		-7		24.1	25.1
	8		21.6	20.7		7		25.9	- 26.2	-1	0	1	9.0	- 9.7		-8		15.3	- 15.0
	9		34.1	33.9		8		13.9	- 14.2		1		34.3	33.2		-9		7.5	- 7.7
	10		4.0	- 3.2	5	0	1	13.2	- 12.4		2		35.0	33.0	-4	-1	1	21.2	- 22.4
-3	1	0	25.8	23.1		1		8.5	9.9		3		142.5	157.8		-2		21.1	19.5
	2		53.5	53.6		2		83.4	- 86.6		4		36.6	38.4		-3		26.1	23.7
	3		32.9	37.2		3		72.3	- 73.6		5		51.1	- 48.6		-4		14.9	- 16.3
	4		37.6	42.0		4		8.7	- 9.1		6		45.3	43.2		-5		2.1	3.7
	5		3.8	- 2.6		5		3.3	- 1.9		7		19.3	21.1		-6		22.6	23.3
	6		24.6	23.8		6		15.3	15.9		8		4.6	- 3.7		-7		34.0	34.4

Table 2. *(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
-4	-8	1	6.1	4.4	1	-8	2	28.1	- 28.0	-5	6	2	2.5	- 2.7	3	5	3	8.1	7.9
-5	-1	1	74.6	- 77.0		-9		23.7	23.6		7		54.6	- 55.5		6		15.5	- 15.3
	-2		23.3	- 22.6		-10		1.3	- 1.5		8		1.5	- 1.3		7		9.6	- 12.1
	-3		39.9	39.8	2	-1	2	42.8	44.9	-6	0	2	14.8	15.5	4	0	3	19.7	- 19.7
	-4		25.9	- 26.0		-2		13.4	- 12.3		1		7.1	7.7		1		4.4	- 0.3
	-5		18.4	- 19.0		-3		86.0	- 89.1		2		57.3	- 58.7		2		61.9	63.2
	-6		31.3	30.0		-4		51.4	- 53.1		3		51.4	- 51.8		3		40.8	40.9
	-7		18.6	17.7		-5		52.3	- 52.1		4		34.8	- 33.5		4		5.4	3.5
-6	-1	1	61.1	- 61.2		-6		18.7	- 18.5		5		41.2	- 41.6		5		6.6	- 7.1
	-2		18.7	19.0		-7		51.3	- 51.3		6		3.0	1.7		6		17.2	- 17.2
	-3		63.3	64.4		-8		58.1	- 58.3		7		21.7	- 21.0	5	0	3	13.6	- 12.2
	-4		18.8	- 18.2		-9		58.0	58.6	-7	0	2	31.9	30.5		1		9.7	10.1
	-5		20.9	- 20.2		-10		38.1	37.6		1		26.1	25.3		2		13.1	- 14.7
	-6		6.2	5.2	3	-1	2	92.1	98.5		2		38.5	- 38.9		3		9.2	7.2
-7	-1	1	9.1	- 9.3		-2		33.4	31.8		3		4.6	- 2.9		4		13.9	14.1
	-2		57.2	58.2		-3		41.0	- 42.3		4		53.7	55.0		5		13.8	- 12.6
	-3		48.2	48.2		-4		2.6	- 2.1		5		2.1	- 3.5	6	0	3	2.7	0.7
	-4		15.5	16.1		-5		12.2	- 10.3	-1	-1	2	99.4	-104.2		1		8.2	- 6.4
-8	-1	1	6.4	7.2		-6		17.9	- 16.3		-2		45.4	46.2		2		17.8	- 16.6
0	0	2		7.5		-7		12.2	- 13.3		-3		2.0	- 6.0		3		2.6	2.2
	1		15.5	12.6		-8		53.0	- 54.3		-4		59.1	- 58.3	7	0	3	40.4	41.0
	2		11.5	15.7		-9		17.8	17.9		-5		5.0	- 5.6	0	-1	3		- 59.5
	3		48.8	49.6		-10		15.6	17.1		-6		16.5	17.0		-2		30.6	- 31.0
	4		13.5	- 13.1	4	-1	2	132.7	144.8		-7		41.5	41.3		-3		39.3	35.8
	5		36.6	- 32.9		-2		16.3	15.2		-8		1.1	- 2.0		-4		74.7	- 73.4
	6		43.3	45.0		-3		4.7	- 6.5		-9		41.6	- 42.7		-5		38.6	- 38.7
	7		12.6	11.6		-4		37.4	38.2		-10		18.7	16.6		-6		6.0	- 4.6
	8		25.3	- 25.0		-5		40.8	42.4	-2	-1	2	54.9	- 62.0		-7		4.9	7.2
	9		8.3	- 8.7		-6		9.8	- 10.4		-2		25.2	23.5		-8		49.2	50.7
1	0	2	43.8	42.9		-7		53.7	- 54.4		-3		27.7	25.5		-9		8.9	- 9.1
	1		45.9	44.0		-8		42.6	- 42.5		-4		60.5	- 59.5	1	-1	3	53.2	- 58.3
	2		32.7	33.6		-9		14.8	- 15.3		-5		12.7	- 13.2		-2		41.8	- 39.8
	3		53.3	57.8	5	-1	2	36.9	38.5		-6		59.1	59.2		-3		26.4	23.8
	4		3.4	- 1.2		-2		24.0	24.6		-7		59.7	61.2		-4		62.7	- 61.8
	5		4.4	1.1		-3		36.5	37.1		-8		18.3	17.5		-5		20.0	- 22.1
	6		32.5	33.5		-4		23.6	24.1		-9		16.5	- 17.2		-6		41.4	42.2
	7		35.0	- 33.9		-5		14.4	14.4	-3	-1	2	55.5	- 56.4		-7		3.5	7.0
	8		15.7	- 15.5		-6		24.7	- 24.3		-2		69.2	- 69.2		-8		41.8	42.1
	9		25.2	- 25.4		-7		39.9	- 39.4		-3		42.8	43.5		-9		6.9	5.6
2	0	2	6.1	- 1.1		-8		1.8	- 1.1		-4		7.8	9.7	2	-1	3	24.8	- 25.8
	1		82.6	- 79.8		-9		25.7	- 27.1		-5		17.9	- 19.2		-2		26.2	24.5
	2		27.2	- 20.5	6	-1	2	6.3	6.3		-6		14.1	15.1		-3		27.2	25.2
	3		92.0	95.9		-2		6.7	7.1		-7		29.6	30.8		-4		22.1	- 22.4
	4		6.4	8.7		-3		19.0	19.6		-8		23.1	22.8		-5		37.3	- 38.4
	5		3.3	- 0.6		-4		18.7	18.1		-9		18.3	18.7		-6		41.9	41.6
	6		9.8	9.5		-5		27.8	27.1	-4	-1	2	40.7	- 42.9		-7		15.8	16.6
	7		1.9	0.1		-6		22.6	- 23.7		-2		18.6	- 18.1		-8		28.2	- 30.1
	8		42.7	43.2		-7		34.1	- 33.3		-3		28.1	30.1		-9		2.6	3.4
	9		31.0	- 28.9	7	-1	2	10.8	- 10.6		-4		5.3	8.5	3	-1	3	60.0	59.8
3	0	2	19.3	19.1		-2		20.2	- 19.2		-5		17.5	- 18.0		-2		29.3	29.7
	1		53.4	- 52.1		-3		21.9	21.3		-6		4.9	3.9		-3		15.3	- 16.6
	2		10.3	10.1		-4		8.3	6.8		-7		5.4	4.3		-4		31.8	- 33.6
	3		22.3	23.1		-5		4.6	3.3		-8		16.8	- 19.1		-5		43.3	- 42.8
	4		4.7	- 3.3		-6		20.4	20.5	-5	-1	2	10.3	- 11.2		-6		1.4	1.1
	5		12.6	- 12.3	-1	0	2	74.7	- 83.9		-2		14.2	13.0		-7		28.2	- 27.0
	6		25.4	- 23.7		1		3.0	1.6		-3		60.5	61.9		-8		83.5	- 86.8
	7		36.1	36.3		2		19.8	- 13.4		-4		48.8	51.0		-9		4.5	- 4.3
	8		25.8	25.6		3		5.5	4.5		-5		24.2	25.2	4	-1	3	42.5	42.3
4	0	2	67.5	69.2		4		26.8	- 25.9		-6		23.3	24.9		-2		27.4	27.2
	1		15.5	- 16.0		5		22.7	23.9		-7		1.9	0.6		-3		28.7	- 30.4
	2		6.9	5.1		6		102.2	104.6	-6	-1	2	2.0	- 1.2		-4		37.6	- 38.3
	3		27.7	- 25.0		7		50.5	51.2		-2		28.1	26.3		-5		35.4	- 35.5
	4		13.7	14.7		8		3.4	- 2.0		-3		60.9	61.6		-6		8.1	- 7.6
	5		44.0	- 43.5		9		18.2	18.1		-4		32.7	32.2		-7		4.4	- 4.1
	6		63.2	- 64.3	-2	0	2	112.7	-126.3		-5		21.8	21.5		-8		48.9	- 47.9
	7		26.6	28.4		1		66.9	- 66.4	-7	-1	2	15.0	15.9		-9		3.7	- 2.2
5	0	2	37.8	39.1		2		38.9	37.9		-2		3.4	2.4	5	-1	3	7.2	9.1
	1		29.7	27.6		3		10.8	- 15.2		-3		2.9	- 6.6		-2		23.8	24.3
	2		2.2	1.8		4		16.0	- 17.2	0	0	3		- 26.2		-3		35.1	- 36.4
	3		31.2	- 30.4		5		47.2	47.4		1		26.7	- 24.6		-4		1.8	- 1.8
	4		28.4	- 28.1		6		68.6	68.9		2		40.9	37.3		-5		6.0	6.9
	5		51.9	- 51.9		7		54.0	53.3		3		10.4	- 10.4		-6		10.1	- 9.9
	6		40.5	- 39.3		8		4.8	3.8		4		19.4	18.5		-7		16.4	16.2
6	0	2	56.6	58.0		9		6.7	7.4		5		65.8	66.1		-8		14.5	- 13.8
	1		16.3	16.7	-3	0	2	36.4	- 37.9		6		77.6	78.6	6	-1	3	11.6	9.8
	2		26.9	- 25.7		1		44.9	- 43.5		7		57.9	57.8		-2		25.0	25.4
	3		6.2	5.9		2		30.8	34.3		8		11.6	- 11.3		-3		2.3	- 2.1
	4		2.6	- 2.2		3		59.2	- 58.1	1	0	3	12.2	- 16.8		-4		6.2	6.2
	5		15.5	- 14.9		4		5.5	- 9.5		1		28.5	- 27.8		-5		30.0	28.5
7	0	2	11.1	9.9		5		70.8	69.6		2		8.7	- 7.8		-6		2.1	- 1.3
	1		21.6	- 20.9		6		7.7	2.0		3		5.1	- 4.1	7	-1	3	40.8	38.1
	2		20.5	- 18.4		7		9.9	9.2		4		24.2	- 21.8		-2		3.7	1.3
	3		7.3	- 4.6		8		1.9	0.7		5		33.4	33.8		-3		38.4	40.5
0	-1	2	19.8	20.4		9		20.1	19.2		6		85.6	86.3		-4		36.0	36.0
	-2		60.5	61.6	-4	0	2	6.7	5.6		7		19.2	19.5	-1	0	3	63.8	- 64.9
	-3		25.8	23.0		1		15.6	- 13.2		8		13.1	14.0		1		43.2	- 47.2
	-4		30.9	- 36.5		2		8.5	7.8	2	0	3	23.7	- 23.8		2		27.9	- 26.3
	-5		14.7	11.0		3		16.7	- 18.1		1		20.7	19.8		3		29.5	- 30.9
	-6		30.4	30.4		4		52.7	- 54.1		2		45.4	46.5		4		13.4	10.6
	-7		21.8	- 21.0		5		18.3	18.5		3		16.0	16.1		5		9.2	10.2
	-8		34.8	- 35.6		6		1.6	1.9		4		80.0	- 79.3		6		1.5	3.9
	-9		23.9	- 23.1		7		16.7	- 17.5		5		1.9	0.0		7		39.1	38.8
	-10		13.7	11.8		8		13.0	13.4		6		54.0	54.0		8		3.7	0.3
1	-1	2	3.7	1.7		9		24.3	23.7		7		14.5	- 15.4	-2	0	3	26.4	- 25.1
	-2		19.6	- 17.3	-5	0	2	46.5	46.3		8		1.0	0.3		1		3.0	2.5
	-3		56.9	50.2		1		9.4	9.6	3	0	3	18.9	15.3		2		65.8	- 67.9
	-4		2.7	- 9.7		2		93.2	- 94.2		1		9.2	8.9		3		95.3	- 99.0
	-5		63.3	- 62.7		3		46.7	- 47.5		2		85.8	86.5		4		32.8	- 31.4
	-6		14.7	- 13.1		4		76.0	- 76.3		3		59.3	60.4		5		8.0	8.5
	-7		59.0	- 61.1		5		33.8	- 33.1		4		12.9	- 11.7		6		15.6	- 14.7

Table 2. *(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
-2	7	3	18.8	- 18.8	0	5	4	13.9	- 13.6	-1	2	5	54.9	- 53.2	2	1	5	45.3	- 44.4
	8		14.4	13.5		6		9.8	- 10.6		3		37.4	- 36.2		2		64.4	- 65.3
-3	0	3	47.0	48.3		7		2.5	1.6		4		12.6	- 12.7		3		22.6	- 22.8
	1		26.8	- 26.8	1	0	4	2.6	- 4.2		5		3.8	5.2		4		24.9	- 26.4
	2		63.0	- 66.5		1		21.2	21.0		6		18.2	- 16.9	3	0	5	2.4	2.6
	3		71.4	- 72.3		2		39.1	- 39.1		7		18.5	18.4		1		39.5	- 40.0
	4		22.4	- 24.7		3		34.7	- 34.3	-2	0	4	1.7	2.2		2		14.7	- 13.3
	5		20.9	19.9		4		7.8	8.8		1		7.6	- 10.0		3		9.4	- 8.8
	6		30.0	- 29.2		5		5.0	4.8		2		51.8	- 50.9	4	0	5	2.0	- 3.1
	7		28.9	- 29.3		6		9.0	9.0		3		30.2	- 28.6		1		14.0	13.8
	8		40.0	39.3		7		38.4	- 40.3		4		3.6	- 2.6		2		15.1	15.4
-4	0	3	33.3	34.2	2	0	4	26.3	- 26.5		5		6.0	7.6	0	-1	5		27.0
	1		20.8	- 20.4		1		3.0	5.2		6		12.8	- 12.4		-2		5.1	- 9.3
	2		74.0	- 73.3		2		19.2	19.0		7		13.7	- 14.7		-3		42.1	- 43.2
	3		39.3	- 38.8		3		4.3	- 6.1	-3	0	4	61.7	59.5		-4		26.9	28.4
	4		9.1	- 8.9		4		16.5	17.7		1		22.1	- 21.7		-5		50.5	51.7
	5		37.2	35.6		5		70.2	71.5		2		15.3	- 14.1		-6		6.6	- 10.1
	6		5.3	5.5		6		50.3	49.4		3		31.1	30.4		-7		6.7	- 6.2
	7		35.7	- 36.1	3	0	4	16.3	- 16.3		4		12.1	11.8	1	-1	5	16.0	- 15.6
	8		28.1	28.5		1		29.7	- 29.4		5		3.0	3.2		-2		9.1	- 9.3
-5	0	3	7.2	6.5		2		31.7	31.6		6		18.3	- 16.3		-3		14.5	- 15.2
	1		3.3	1.5		3		2.8	- 3.4		7		29.9	- 30.6		-4		37.4	38.7
	2		31.8	- 31.3		4		17.5	18.2	-4	0	4	65.7	63.5		-5		59.3	59.9
	3		49.2	46.8		5		83.7	84.5		1		32.4	- 32.3		-6		20.6	22.3
	4		18.7	17.1		6		42.1	42.7		2		5.9	7.2		-7		14.7	15.7
	5		15.5	- 14.7	4	0	4	27.7	- 27.0		3		44.2	43.8	2	-1	5	61.2	- 63.8
	6		22.5	23.2		1		6.0	- 9.3		4		20.8	- 21.2		-2		33.7	- 33.7
	7		26.1	- 26.0		2		32.8	33.0		5		31.5	- 30.4		-3		28.7	30.0
-6	0	3	47.2	48.1		3		3.3	3.1		6		29.4	- 27.3		-4		43.4	46.0
	1		35.6	35.3		4		3.8	4.0	-5	0	4	5.4	4.9		-5		45.2	47.7
	2		2.0	0.4		5		20.9	20.7		1		37.4	- 36.6		-6		11.7	12.0
	3		37.5	37.6	5	0	4	21.3	- 20.0		2		17.9	- 18.1		-7		16.2	16.8
	4		26.4	25.6		1		27.9	27.0		3		15.7	15.2	3	-1	5	12.7	- 12.8
	5		31.9	- 32.4		2		24.7	22.6		4		29.1	- 25.5		-2		16.2	- 15.5
-7	0	3	22.2	20.7		3		4.6	3.3		5		56.8	- 58.4		-3		31.5	33.4
	1		3.8	- 4.6	6	0	4	9.6	- 8.3	-6	0	4	9.3	- 9.4		-4		15.5	15.0
	2		10.3	10.4		1		9.6	8.4		1		2.6	- 1.8		-5		7.2	5.5
	3		15.8	14.7	0	-1	4		- 53.2		2		1.4	- 4.1		-6		5.3	5.8
-1	-1	3	35.7	- 40.3		-2		3.7	0.6		3		16.2	15.6	4	-1	5	7.0	7.9
	-2		4.0	- 3.3		-3		31.7	30.3	-1	-1	4	0.6	- 1.6		-2		44.5	- 46.9
	-3		5.9	- 5.6		-4		34.1	33.7		-2		5.8	- 7.8		-3		6.4	- 6.2
	-4		3.5	- 1.0		-5		50.1	48.7		-3		21.1	- 19.6		-4		9.7	11.5
	-5		16.8	- 18.2		-6		5.5	6.4		-4		64.0	62.1		-5		46.4	- 50.6
	-6		21.2	- 21.5		-7		32.0	31.6		-5		60.6	59.3	-1	0	5	2.1	1.6
	-7		27.4	28.9		-8		26.8	26.8		-6		22.8	21.1		1		30.8	- 31.3
	-8		14.1	13.7	1	-1	4	60.2	- 63.8		-7		41.5	40.2		2		1.9	2.1
	-9		1.4	- 0.6		-2		33.1	- 32.7		-8		6.1	4.0		3		12.7	12.8
-2	-1	3	42.9	- 45.0		-3		45.5	42.7	-2	-1	4	25.9	27.4		4		2.3	- 0.2
	-2		19.8	- 18.7		-4		36.3	34.3		-2		14.9	- 15.4		5		13.2	- 11.6
	-3		47.3	47.7		-5		2.1	- 0.9		-3		13.7	- 13.5	-2	0	5	18.9	18.5
	-4		91.4	95.4		-6		3.6	- 2.0		-4		69.3	68.0		1		21.4	- 21.0
	-5		3.5	2.5		-7		22.5	21.6		-5		12.0	11.3		2		10.7	9.7
	-6		15.2	- 14.6		-8		49.0	47.3		-6		14.2	14.7		3		11.2	- 11.4
	-7		33.1	32.8	2	-1	4	76.4	- 80.0		-7		31.7	31.4		4		17.0	- 16.2
	-8		4.4	3.0		-2		72.0	- 71.2		-8		6.6	5.2		5		19.9	- 19.0
	-9		5.6	- 6.5		-3		21.5	20.9	-3	-1	4	58.4	56.7	-3	0	5	4.6	- 5.7
-3	-1	3	22.5	20.4		-4		31.9	- 30.7		-2		15.4	- 15.1		1		16.7	- 15.5
	-2		20.3	- 21.5		-5		78.4	- 78.6		-3		3.1	3.5		2		36.2	35.8
	-3		77.9	81.9		-6		2.5	2.6		-4		14.5	13.6		3		2.5	1.2
	-4		104.7	110.3		-7		25.0	24.3		-5		2.6	- 2.1		4		32.1	- 32.3
	-5		39.0	40.2		-8		30.5	27.4		-6		16.3	- 16.5	-4	0	5	10.0	8.6
	-6		30.5	31.3	3	-1	4	46.6	- 48.0		-7		52.4	- 52.3		1		10.1	- 11.7
	-7		20.3	19.9		-2		87.6	- 93.7	-4	-1	4	44.9	43.0		2		33.8	32.2
	-8		2.6	2.2		-3		3.8	- 0.5		-2		17.0	15.0		3		51.9	53.1
-4	-1	3	19.9	- 18.4		-4		27.0	- 26.7		-3		41.0	40.4	-5	0	5	4.0	3.5
	-2		32.9	- 33.2		-5		49.2	- 48.9		-4		7.5	- 8.5		-1		34.5	33.1
	-3		45.0	46.0		-6		15.8	14.3		-5		13.9	13.4		-2		7.8	7.2
	-4		62.0	65.1		-7		12.5	11.4		-6		4.4	- 6.9		-3		13.1	- 13.5
	-5		16.1	16.9		-8		12.7	11.8	-5	-1	4	20.8	20.8		-4		8.4	8.7
	-6		20.9	21.3	4	-1	4	15.7	16.3		-2		25.8	25.7		-5		5.5	6.3
	-7		8.8	10.1		-2		3.9	- 5.1		-3		12.1	12.2		-6		6.8	- 8.5
-5	-1	3	10.3	- 9.7		-3		7.8	9.1		-4		10.1	- 9.2	-2	-1	5	54.1	55.2
	-2		16.0	15.8		-4		18.2	17.3		-5		36.9	37.4		-2		10.0	- 10.6
	-3		2.8	3.4		-5		5.6	- 6.7	-6	-1	4	4.4	2.4		-3		31.5	31.5
	-4		6.3	- 6.1		-6		27.8	27.7		-2		9.7	8.6		-4		45.1	46.8
	-5		0.7	- 1.7		-7		17.9	17.3	0	0	5	19.8	21.5		-5		7.5	6.1
	-6		1.9	- 2.6	5	-1	4	18.0	19.4		1		14.5	- 15.6		-6		26.0	28.0
-6	-1	3	19.3	19.5		-2		41.8	42.9		2		42.0	- 41.5	-3	-1	5	20.3	19.6
	-2		24.4	25.3		-3		4.1	5.9		3		16.7	18.4		-2		3.1	- 4.2
	-3		12.0	13.0		-4		23.3	24.5		4		49.3	49.4		-3		34.6	36.3
	-4		2.6	- 2.1		-5		15.9	- 14.7		5		3.7	- 2.2		-4		1.5	1.1
-7	-1	3	31.3	31.3		-6		23.5	- 23.1	1	0	5	7.9	- 8.3		-5		2.1	2.0
	-2		15.9	15.2	6	-1	4	15.5	14.7		1		26.6	- 26.5	-4	-1	5	3.8	- 6.4
0	0	4		- 14.1		-2		61.1	61.2		2		52.0	- 51.6		-2		3.3	1.9
	1		9.0	- 11.7		-3		2.4	- 2.4		3		14.0	15.4		-3		19.0	- 20.7
	2		42.5	- 42.3		-4		37.9	- 36.4		4		21.4	20.2		-4		64.5	- 68.8
	3		39.7	- 39.3	-1	0	4	3.8	- 4.0		5		6.4	- 6.1					
	4		15.3	- 14.7		1		25.5	- 25.8	2	0	5	2.2	1.2					

all 1141 reflections were included. The resulting R value for all reflection proved to be 5.4%.

Table 2 gives the observed and calculated structure factors. Table 3 shows the final parameters of the nonhydrogen atoms. The

Table 3. *Final parameters of the nonhydrogen atoms of amarantite*

Atom	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	B
Fe(1)	.9128	(2)	.9361	(1)	.1442	(2)	1.9 Å^2
Fe(2)	.9259	(2)	.2369	(1)	.2250	(2)	2.0
S(1)	.8322	(2)	.6508	(2)	.0794	(3)	.4
S(2)	.2113	(2)	.9325	(2)	.4461	(3)	.4
O(1)	.0250	(6)	.3415	(5)	.0353	(9)	1.7
O(2)	.2930	(7)	.4066	(5)	.0473	(9)	1.6
O(3)	.8038	(6)	.7719	(5)	.1465	(8)	1.0
O(4)	.8523	(7)	.5931	(5)	.2590	(9)	1.7
O(5)	.8321	(6)	.9630	(5)	.4341	(8)	.7
O(6)	.7809	(6)	.1609	(5)	.4182	(8)	1.3
O(7)	.3542	(6)	.9589	(5)	.3537	(9)	1.5
O(8)	.0919	(6)	.8889	(5)	.2922	(9)	.9
O(9)	.9863	(6)	.0955	(4)	.1119	(8)	.7
O(10)	.5355	(7)	.7786	(5)	.3971	(9)	1.9
O(11)	.8831	(7)	.3872	(5)	.3945	(9)	1.7
O(12)	.7375	(7)	.2333	(5)	.0482	(9)	1.8
O(13)	.2815	(7)	.6249	(5)	.2616	(9)	1.9
O(14)	.7039	(6)	.9606	(5)	.0272	(9)	1.5
O(15)	.4551	(7)	.2339	(6)	.1879	(9)	2.1
O(16)	.1150	(6)	.2519	(5)	.4085	(8)	1.1

temperature coefficients given in this table are the isotropic equivalents of the final anisotropic temperature coefficients, calculated according to HAMILTON[7]. Table 4 lists the interatomic distances and angles. The standard deviations are: for Fe—Fe: 0.003 Å, for Fe—O and S—O: 0.006 Å, for O—O: 0.01 Å, for Fe—O—Fe and O—Fe—O: 0.2°, and for O—S—O, S—O—O and O—O—O: 0.3°.

Description of the structure

The Fe atoms are surrounded octahedrally by oxygen atoms. As will be shown later, some of the oxygen atoms surrounding Fe are oxygen atoms of water molecules. In Table 4 they are assigned by w's. The average Fe(1)—O distance is 2.05 Å, the individual distances lying between 1.95 and 2.09 Å. In the case of Fe(2) the corresponding values are 2.03, 1.89, and 2.07 Å. The sulfate groups have the normal tetrahedral form. In both tetrahedra the average S—O distance is 1.47 Å. Two centrosymmetrical pairs of octahedra and tetrahedra are connected to a group of composition $Fe_4S_4O_{28}$

[7] W. C. HAMILTON, On the isotropic temperature factor equivalent to a given anisotropic temperature factor. Acta Crystallogr. **12** (1959) 609—610.

Table 4. *Interatomic distances and angles*

	Atoms			Angles	Distances		
	A	B	C	ABC	AB	AC	BC
Fe(1)	O(9)	Fe(1)	O(8)	100.3°	1.929 Å	3.05 Å	2.045 Å
octahedron	O(8)		O(3)	89.8	2.045	2.89	2.042
	O(3)		O(14)*w*	80.5	2.042	2.67	2.091
	O(14)*w*		O(9)	89.6	2.091	2.83	1.929
	O(8)		O(5)	82.8	2.045	2.73	2.085
	O(5)		O(14)*w*	89.8	2.085	2.95	2.091
	O(14)*w*		O($\overline{9}$)	98.0	2.091	3.07	1.969
	O($\overline{9}$)		O(8)	89.3	1.969	2.82	2.045
	O($\overline{9}$)		O(3)	95.2	1.969	2.96	2.042
	O(3)		O(5)	84.9	2.042	2.79	2.085
	O(5)		O(9)	97.5	2.085	3.02	1.929
	O(9)		O($\overline{9}$)	83.7	1.929	2.60	1.969
	O($\overline{9}$)		O(5)	172.1	1.969		2.085
	O(3)		O(9)	169.8	2.042		1.929
	O(14)*w*		O(8)	168.3	2.091		2.045
Fe(2)	O(9)	Fe(2)	O(1)	98.9°	1.892 Å	2.95 Å	1.986 Å
octahedron	O(1)		O(11)*w*	85.9	1.986	2.77	2.074
	O(11)*w*		O(6)	82.6	2.074	2.71	2.028
	O(6)		O(9)	94.4	2.028	2.88	1.892
	O(16)*w*		O(1)	93.3	2.069	2.95	1.986
	O(1)		O(12)*w*	85.2	1.986	2.73	2.052
	O(12)*w*		O(6)	84.3	2.052	2.74	2.028
	O(6)		O(16)*w*	96.5	2.028	3.06	2.069
	O(16)*w*		O(11)*w*	88.5	2.069	2.77	2.074
	O(11)*w*		O(12)*w*	92.4	2.074	2.98	2.052
	O(12)*w*		O(9)	91.8	2.052	2.96	1.892
	O(9)		O(16)*w*	86.3	1.892	2.71	2.069
	O(16)*w*		O(12)*w*	175.3	2.069		2.052
	O(9)		O(11)*w*	169.4	1.892		2.074
	O(6)		O(1)	164.0	2.082		1.986
S(1)	O(1)	S(1)	O(2)	110.7°	1.496 Å	2.32 Å	1.456 Å
tetra-	O(2)		O(3)	109.2	1.456	2.41	1.495
hedron	O(3)		O(4)	107.3	1.495	2.38	1.456
	O(4)		O(1)	109.2	1.456	2.41	1.496
	O(1)		O(3)	107.5	1.496	2.41	1.495
	O(2)		O(4)	112.7	1.456	2.42	1.456
S(2)	O(5)	S(2)	O(6)	108.7°	1.489 Å	2.42 Å	1.495 Å
tetra-	O(6)		O(7)	110.1	1.495	2.50	1.439
hedron	O(7)		O(8)	111.0	1.439	2.41	1.489
	O(8)		O(5)	109.1	1.489	2.43	1.489
	O(5)		O(7)	110.8	1.489	2.41	1.439
	O(6)		O(8)	107.1	1.495	2.40	1.489

Table 4. *(Continued)*

	Atoms			Angles	Distances		
	A	B	C	ABC	AB	AC	BC
oxygen environment	Fe(2)	O(1)	S(1)	136.0°	1.986 Å		1.496 Å
	S(1)	O(2)	O(13)	121.5	1.456		2.81
	S(1)		O(15)	108.7	1.456		2.86
	O(13)		O(15)	123.1	2.81		2.86
	Fe(1)	O(3)	S(1)	137.7	2.042		1.495
	Fe(1)		O(10)	109.3	2.042		2.95
	S(1)		O(10)	112.4	1.495		2.95
	S(1)	O(4)	O(11)	144.1	1.456		2.70
	S(1)		O(16)	111.1	1.456		2.72
	O(11)		O(16)	104.7	2.70		2.72
	Fe(1)	O(5)	S(2)	132.6	2.085		1.489
	Fe(1)		O(16)	100.6	2.085		2.91
	S(2)		O(16)	125.7	1.489		2.91
	Fe(2)	O(6)	S(2)	134.1	2.028		1.495
	S(2)	O(7)	O(10)	109.1	1.439		2.85
	S(2)		O(14)	107.2	1.439		2.87
	O(10)		O(14)	122.7	2.85		2.87
	Fe(1)	O(8)	S(2)	142.8	2.045		1.489
	Fe($\bar{1}$)	O(9)	Fe(1)	96.3	1.969	2.903 Å	1.929
	Fe(2)		Fe(1)	128.4	1.892		1.929
	Fe($\bar{1}$)		Fe(2)	131.9	1.969		1.892
	O(3)	O(10)	O(15)	122.6	2.95		2.80
	O(3)		O(13)	116.0	2.95		2.81
	O(3)		O(7)	117.7	2.95		2.85
	O(7)		O(15)	103.4	2.85		2.80
	O(7)		O(13)	86.0	2.85		2.81
	O(13)		O(15)	104.4	2.81		2.80
	Fe(2)	O(11)	O(13)	120.4	2.074		2.75
	Fe(2)		O(4)	126.9	2.074		2.70
	O(13)		O(4)	106.8	2.75		2.70
	Fe(2)	O(12)	O(15)	124.7	2.052		2.71
	Fe(2)		O(13)	123.7	2.052		2.80
	O(15)		O(13)	98.8	2.71		2.80

Table 4. *(Continued)*

Atoms			Angles	Distances		
A	B	C	ABC	AB	AC	BC
O(10)	O(13)	O(2)	124.2°	2.81 Å		2.81 Å
O(10)		O(11)	101.8	2.81		2.75
O(10)		O(12)	86.2	2.81		2.80
O(12)		O(2)	101.9	2.80		2.81
O(12)		O(11)	129.4	2.80		2.75
O(11)		O(2)	113.0	2.75		2.81
Fe(1)	O(14)	O(7)	126.8	2.091		2.87
Fe(1)		O(15)	115.5	2.091		2.79
O(7)		O(15)	103.3	2.87		2.79
O(14)	O(15)	O(2)	98.3	2.79		2.86
O(14)		O(12)	103.2	2.79		2.71
O(14)		O(10)	113.9	2.79		2.80
O(2)		O(12)	115.0	2.86		2.71
O(2)		O(10)	116.9	2.86		2.80
O(12)		O(10)	108.4	2.71		2.80
Fe(2)	O(16)	O(5)	114.1	2.069		2.91
Fe(2)		O(4)	120.8	2.069		2.72
O(5)		O(4)	102.6	2.91		2.72

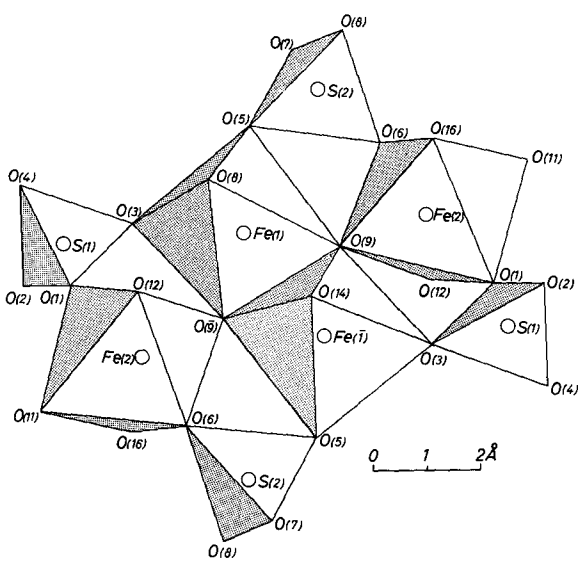

Fig. 1. Group of octahedra and tetrahedra with composition $Fe_4S_4O_{28}$

(Fig. 1). Within a group, two Fe(1) octahedra share an edge. This causes the Fe atoms to approach to a distance of 2.90 Å. The $Fe_4S_4O_{28}$ groups are connected by O(8) to form chains parallel to the c axis (Fig. 2). As will be shown later, these chains are linked to each other only by hydrogen bonds.

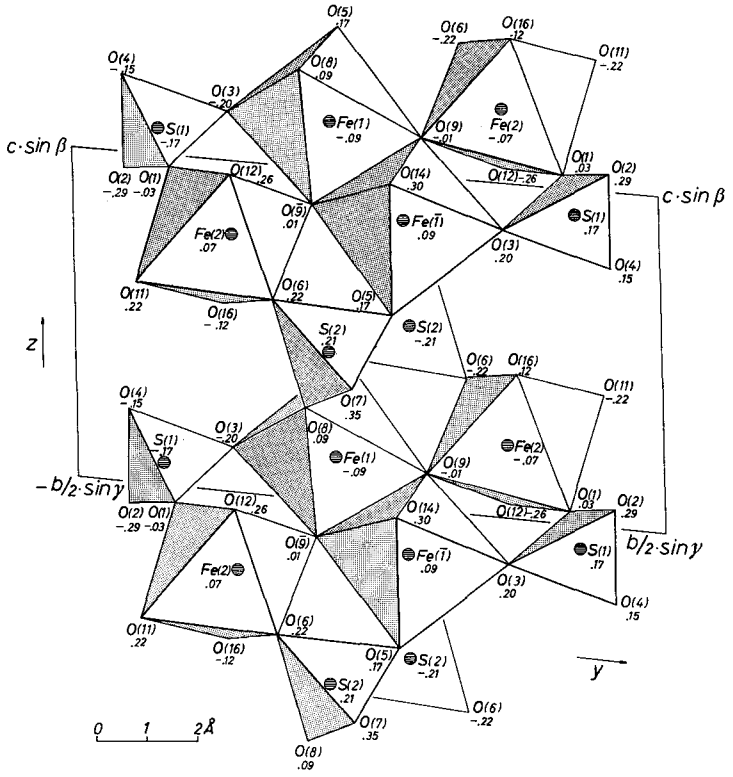

Fig. 2. Chain of octahedra and tetrahedra parallel to the c axis, projected along the a axis. Next to each atom is given its designation and its x coordinate

The bond angles and distances between each oxygen atom and its neighbors are also listed in Table 4. Four oxygen atoms have only cation neighbors, three oxygen atoms are surrounded only by oxygen, and the rest have a mixed environment of cations and oxygen. The most remarkable oxygen atom is O(9); this is located almost in the center of the Fe($\bar{1}$)—Fe(1)—Fe(2) triangle. The oxygen atom next to O(9), and not belonging to the same octahedron, is farther away than 3.5 Å. The three bond angles Fe—O(9)—Fe are rather different from the ideal angle of 120° (which, for example, occur in the rutile struc-

ture) but their sum is also near 360°. The three oxygen atoms not bonded to cations are surrounded tetrahedrally by four oxygen atoms with bond angles ranging from 86° to 124°. As can be seen in Table 4, there are 14 different oxygen-oxygen pairs whose O—O distances fall in the range from 2.70 to 2.95 Å.

The hydrogen-bond system

Since there are just 14 hydrogen atoms in the structure, they can be assumed to be located somewhere between the partners of the 14 oxygen pairs. If the sulfate oxygen atoms O(2), O(3), O(4), O(5) and O(7) are regarded as proton acceptors, the system of hydrogen bonds O···H—O illustrated in Fig. 3 follows unequivocally. This was confirmed by the final three-dimensional difference-Fourier synthesis which led to the determination of probable positions for the hydrogen atoms whose coordinates are listed in Table 5. When the hydrogen atoms were included in the final structure-factor calculation, the R value dropped from 5.4 to 5.2%.

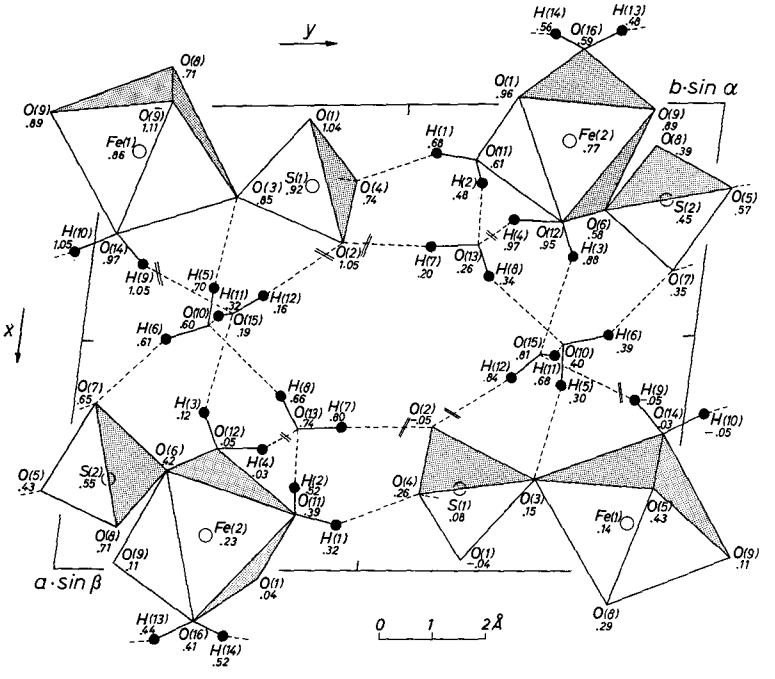

Fig. 3. The crystal structure of amarantite and its hydrogen-bond system projected along the c axis. Next to each atom is given its designation and its z coordinate

Table 5. *Coordinates of the hydrogen atoms*

	x	y	z		x	y	z
H(1)	.88	.46	.32	H(8)	.38	.65	.34
H(2)	.82	.38	.52	H(9)	.35	.11	.05
H(3)	.64	.21	.12	H(10)	.32	.97	.05
H(4)	.73	.31	.03	H(11)	.46	.23	.32
H(5)	.62	.78	.30	H(12)	.42	.29	.16
H(6)	.51	.86	.39	H(13)	.13	.18	.44
H(7)	.29	.54	.20	H(14)	.12	.30	.52

Table 6. *Hydrogen-bond distances and angles*

Atoms			Angles	Distances		
A	B	C	ABC	AB	AC	BC
O(4)	··· H(1)	— O(11)	164°	1.69 Å	2.70Å	1.03 Å
O(13)	··· H(2)	— O(11)	177	1.73	2.75	1.02
H(1)	— O(11)	— H(2)	118	1.03		1.02
O(15)	··· H(3)	— O(12)	150	1.77	2.71	1.02
O(13)	··· H(4)	— O(12)	124	2.17	2.80	.93
H(3)	— O(12)	— H(4)	102	1.02		.93
O(3)	··· H(5)	— O(10)	170	1.96	2.95	1.00
O(7)	··· H(6)	— O(10)	147	1.95	2.85	1.01
H(5)	— O(10)	— H(6)	99	1.00		1.01
O(2)	··· H(7)	— O(13)	167	1.78	2.81	1.05
O(10)	··· H(8)	— O(13)	143	1.92	2.81	1.02
H(7)	— O(13)	— H(8)	104	1.05		1.02
O(15)	··· H(9)	— O(14)	177	1.79	2.79	1.00
O(7)	··· H(11)	— O(14)	130	2.07	2.87	1.05
H(9)	— O(14)	— H(11)	105	1.00		1.05
O(10)	··· H(11)	— O(15)	178	1.90	2.80	.89
O(2)	··· H(12)	— O(15)	166	2.07	2.86	.80
H(11)	··· O(15)	— H(12)	112	.89		.80
O(5)	··· H(13)	— O(16)	168	2.01	2.91	.91
O(4)	··· H(14)	— O(16)	174	1.83	2.72	.89
H(13)	— O(16)	— H(14)	109	.91		.89

Table 6 lists the hydrogen-bond angles and distances. The estimated standard deviations are: 0.15 Å for the distances O—H and O···H, and 20° for the angles H—O—H and O···H—O. The O—H

distances range from 0.80 to 1.05 Å. The angles O···H—O are, in most cases, not far from 180°. Only those of H(4) and H(10) deviate considerably from 180°, but their standard deviations are too large to allow a useful discussion.

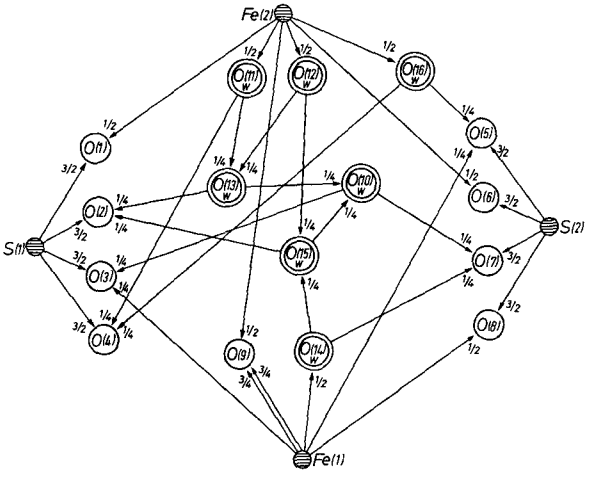

Fig. 4. Electrostatic valency bond scheme of the crystal structure of amarantite

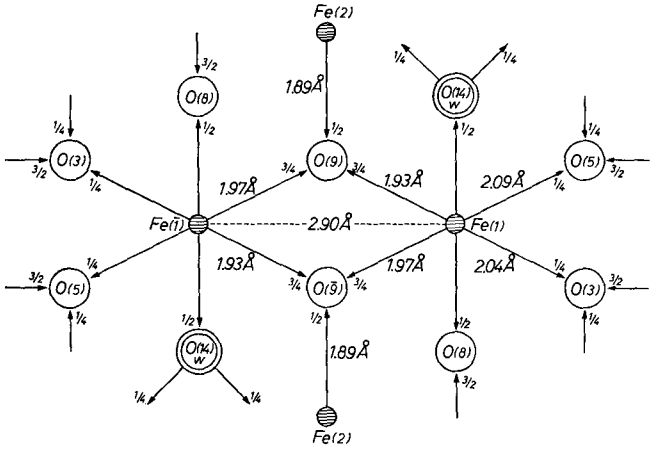

Fig. 5. The electrostatic valency bonds in the neighborhood of Fe(1)

Under the assumption of an entirely ionic structure, an electrostatic valency bond scheme can be developed as shown in Fig. 4. In order to reconcile the bond strengths received by oxygen atoms and water molecules with PAULING's second rule, different electrostatic bond strengths must be assumed around Fe(1). As shown separately in Fig. 5,

O(3) and O(5) can each receive only a bond strength of $\frac{1}{4}$ from Fe(1). Because of this, the excess bond strength of Fe(1) must be donated to some other oxygen atoms. Since O(14) and O(8) are saturated, the excess must be donated to O(9) and O($\bar{9}$). This turns out to be, what they require. The differences in the interatomic distances of the opposite Fe(1)—O pairs appear to support this point of view.

Conclusions

According to this system of hydrogen bonds, no hydroxyl groups exist in the structure. The seven oxygen atoms O(10) to O(16) turn out to be oxygen atoms of water molecules. The oxygen atoms O(1), O(6), O(8) and O(9) are not involved in hydrogen bonds, and the rest of the oxygen atoms are proton acceptors. If these results are accepted, the chemical formula of amarantite should be $Fe_2(SO_4)_2O \cdot 7H_2O$. The former formula $2(Fe(SO_4)OH \cdot 3H_2O)$ does not correspond to the structure reported here.

The crystal structure permits an explanation of some physical properties of the amarantite crystals. The elongation parallel to [001] is due to the relatively strong chains parallel to the c axis in the structure. The perfect cleavage parallel (100) and (010) is the consequence of the fact that the chains are connected to each other only weakly by hydrogen bonds. According to the dehydration curve of amarantite[1], three water molecules are lost easily below 100 °C. These are the three water molecules in the structure located between the chains and not linked to cations.

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