DETERMINATION AND REFINEMENT OF THE CRYSTAL STRUCTURE OF CHAIDAMUITE

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ABSTRACT

Chaidamuite ($ZnFe(SO_4)_2(OH)\cdot 4H_2O$), which is a new sulphate mineral, belongs to the triclinic system, space group $P1$, with the cell parameters corrected by the least-squares method: $a = 7.309(2)$ Å, $b = 7.202(2)$ Å, $c = 9.691(3)$ Å, $\alpha = 89.64(3)°$, $\beta = 105.89(3)°$, $\gamma = 91.11(2)°$, $Z = 2$. The crystal structure has been determined by the Patterson method and Fourier syntheses and refined by the full-matrix least-squares method to an R factor of 0.032, using 2833 independent reflections. In the structure, a zigzag chain consists of $[Fe(1)O_5(OH)]$ and $[Fe(2)O_5(OH)]$ octahedra sharing the OH corners, and an octahedral-tetrahedral chain running parallel to the b axis consists of the zigzag chain of Fe octahedra and (SO_4) tetrahedra sharing four pairs of octahedral corners on either side of the zigzag chains. These chains are cross-linked by the isolated $[Zn(1)O_2(H_2O)_4]$ and $[Zn(2)O_2(H_2O)_4]$ octahedra into corrugated sheets parallel to the (100) plane. Adjacent sheets are hydrogen-bonded through water molecules.

Keywords: Chaidamuite, crystal structure, triclinic, *P*1.

Chaidamuite ($ZnFe(SO_4)_2(OH)\cdot 4H_2O$) is a new sulphate mineral discovered in Qinghai Province, China, in 1983 and similar to guildite in chemical composition[1]. Both of the minerals have been believed to be isostructural, belonging to the monoclinic system, space group $P2_1$. The determination and refinement of the crystal structure of the mineral show that the higher symmetry of arrangement of part of heavy atoms causes $P2_1$ pseudosymmetric component in the structure of Chaidamuite. In reality, the structure of the mineral belongs to the triclinic system, space group $P1$ as a whole.

I. EXPERIMENTAL

A growth-perfect single crystal with dimensions of 0.5 mm × 0.2 mm × 0.4 mm from the Xitieshan Mine was mounted on an ENRAF-NONIUS CAD4 four-circle automatic single crystal diffractometer. When the diffraction intensities of the crystal were collected, the X-ray selected was MoKα ($\lambda = 0.7017$ Å) with a graphite monochromator. At first, 25 reflections were searched out to obtain orientation matrix and initiative cell parameters. The six of all ten reflections arbitrarily selected to

define Laue symmetry agree with Laue group 2/m, while the other four reflections agree only with Laue group $\bar{1}$. Besides, the clear systematic absence with $k = 2n + 1$ was observed within the $0k0$ reflections collected along the b axis. For this reason, it was suspected that there possibly is a pseudosymmetric component in the structure. The supposition has been confirmed by the determination and refinement of the structure. The cell parameters corrected by the least-squares method are shown in Table 1.

Table 1

Crystallographic Data for Chaidamuite

$ZnFe(SO_4)_2(OH) \cdot 4H_2O$		
Triclinic, 1		Space Group $P1$
a: 7.309(2)Å	b: 7.202(2)Å	c: 9.691(3)Å
α: 89.64(3)°	β: 105.89(3)°	γ: 91.11(2)°
V: 490.5Å^3	Z: 2 D_c: 2.724	D_m: 2.722

The intensities of all the reflections in the range of $2° < \theta < 25°$ were measured on the diffractometer using the $\omega/2$ variable scan rate method. 2833 reflections of the total 3072 independent reflections measured at room temperature were observed with I more than 3.0σ.

The interpretation and refinement of the structure was taken on the SPD software system on a PDP 11/44 computer. First, the analysis of the structure was carried out according to the space group $P2_1$ because of the presence of pseudosymmetry in the structure; the intensities of the reflections were averaged on the basis of the equivalent points of the space group $P2_1$[2], too. The overall temperature factor $B = 0.757$ and scale $K = 0.043$ were given with the Wilson statistic method. The statistics of the eight odd-even groups are given in Table 2. $\langle |E^2 - 1| \rangle = 0.874$, approximate to 0.968 of a centric symmetry. A rough model of the structure was obtained by the direct method[3]. Then the 17 positions of the non-hydrogen atoms were found, and the value of R factor rapidly reduced to 0.14. After this the value of R factor came to a standstill. The 17 positions of the other half of atoms have been determined by the translation of 2_1 after the space group $P2_1$ changed for $P1$. The structure for 2833 independent reflections of 34 atoms was refined by three-circle full-matrix corrections using anisotropic temperature factors to a final R factor of 0.032. The positions of only a part of the hydrogen atoms were induced from the difference Fourier syntheses, but those of the rest were added in by the theoretical calculating method. The interatomic distance and bond angles are listed in Table 3.

Table 2

Statistics of Eight Odd-Even Groups

All	eee	oee	eoe	ooe	eeo	oeo	eoo	ooo
0.984	1.257	1.338	0.717	0.572	1.252	1.358	0.749	0.628

Table 3

Interatomic Distances (Å) and Angles (°)

	Fe(1)	Octahedron	
Fe(1)-OH	1.963(5)	OH-Fe(1)-O(1)	90.6(2)
Fe(1)-OH′	2.006(5)	OH-Fe(1)-O(3)′	90.6(2)
Fe(1)-O(1)	1.987(6)	OH-Fe(1)-O(6)	89.1(2)
Fe(1)-O(3)′	2.021(7)	OH-Fe(1)-O(7)	90.7(2)
Fe(1)-O(6)	2.037(5)	OH′-Fe(1)-O(1)	88.4(2)
Fe(1)-O(7)	2.041(5)	OH′-Fe(1)-O(3)′	90.3(3)
Mean	2.008	OH′-Fe(1)-O(6)	88.5(2)
OH-O(1)	2.84	OH′-Fe(1)-O(7)	91.8(2)
OH-O(3)′	2.82	O(1)-Fe(1)-O(6)	91.6(2)
OH-O(6)	2.79	O(6)-Fe(1)-O(3)′	88.9(3)
OH-O(7)	2.85	O(3)′-Fe(1)-O(7)	87.9(3)
OH′-O(1)	2.81	Mean	89.9
OH′-O(3)′	2.82		
OH′-O(6)	2.83		
OH′-O(7)	2.92		
O(1)-O(6)	2.91		
O(6)-O(3)′	2.82		
O(3)′-O(7)	2.80		
Mean	2.85		
	Fe(2)	Octahedron	
Fe(2)-OH	1.987(8)	OH-Fe(2)-O(1)′	89.4(3)
Fe(2)-OH′	2.007(6)	OH-Fe(2)-O(3)	89.3(3)
Fe(2)-O(1)′	1.981(8)	OH-Fe(2)-O(6)′	90.2(3)
Fe(2)-O(3)	2.026(8)	OH-Fe(2)-O(7)′	88.5(3)
Fe(2)-O(6)′	2.035(6)	OH′-Fe(2)-O(1)′	91.7(3)
Fe(2)-O(7)′	2.029(6)	OH′-Fe(2)-O(3)	89.7(3)
Mean	2.011	OH′-Fe(2)-O(6)′	93.0(3)
		OH′-Fe(2)-O(7)′	88.4(3)
OH-O(1)′	2.78	O(1)′-Fe(2)-O(6)′	90.6(3)
OH-O(3)	2.83	O(6)′-Fe(2)-O(3)	88.0(3)
OH-O(6)′	2.85	O(3)-Fe(2)-O(7)′	91.2(3)
OH-O(7)′	2.78	Mean	90.0
OH′-O(1)′	2.85		
OH′-O(3)	2.85		
OH′-O(6)′	2.95		
OH′-O(7)′	2.81		
O(1)′-O(6)′	2.86		
O(6)′-O(3)	2.82		
O(3)-O(7)′	2.89		
Mean	2.84		
	Zn(1)	Octahedron	
Zn(1)-O(2)	2.108(5)	O(2)-Zn(1)-O(W1)	96.5(2)
Zn(1)-O(5)	2.123(6)	O(2)-Zn(1)-O(W2)	89.2(2)
Zn(1)-O(W1)	2.104(8)	O(2)-Zn(1)-O(W3)	90.5(2)

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Zn(1)-O(W2)	2.046(5)	O(2)-Zn(1)-O(W4)	88.6(3)
Zn(1)-O(W3)	2.097(7)	O(5)-Zn(1)-O(W1)	90.2(2)
Zn(1)-O(W4)	2.007(6)	O(5)-Zn(1)-O(W2)	91.2(2)
Mean	2.008	O(5)-Zn(1)-O(W3)	82.7(2)
		O(5)-Zn(1)-O(W4)	90.6(3)
O(2)-O(W1)	3.14	O(W1)-Zn(1)-O(W2)	89.3(3)
O(2)-O(W2)	2.93	O(W2)-Zn(1)-O(W3)	89.0(3)
O(2)-O(W3)	3.01	O(W3)-Zn(1)-O(W4)	88.7(3)
O(2)-O(W4)	2.89	Mean	89.7
O(5)-O(W1)	3.00		
O(5)-O(W2)	2.98		
O(5)-O(W3)	2.80		
O(5)-O(W4)	2.94		
O(W1)-O(W2)	2.88		
O(W2)-O(W3)	2.91		
O(W3)-O(W4)	2.86		
Mean	2.94		
	Zn(2)	Octahedron	
Zn(2)-O(2)′	2.099(5)	O(2)′-Zn(2)-O(W1)′	96.7(3)
Zn(2)-O(5)′	2.177(6)	O(2)′-Zn(2)-O(W2)′	90.6(3)
Zn(2)-O(W1)′	2.101(7)	O(2)′-Zn(2)-O(W3)′	92.5(2)
Zn(2)-O(W2)′	2.085(7)	O(2)′-Zn(2)-O(W4)′	88.0(2)
Zn(2)-O(W3)′	2.084(7)	O(5)′-Zn(2)-O(W1)′	89.0(3)
Zn(2)-O(W4)′	2.136(7)	O(5)′-Zn(2)-O(W2)′	89.7(3)
Mean	2.114	O(5)′-Zn(2)-O(W3)′	81.8(3)
		O(5)′-Zn(2)-O(W4)′	91.6(3)
O(2)′-O(W1)′	3.15	O(W1)′-Zn(2)-O(W2)′	91.3(3)
O(2)′-O(W2)′	2.97	O(W2)′-Zn(2)-O(W3)′	90.0(3)
O(2)′-O(W3)′	3.01	O(W3)′-Zn(2)-O(W4)′	89.0(3)
O(2)′-O(W4)′	2.92	Mean	90.0
O(5)′-O(W1)′	3.00		
O(5)′-O(W2)′	3.01		
O(5)′-O(W3)′	2.78		
O(5)′-O(W4)′	3.08		
O(W1)′-O(W2)′	2.97		
O(W2)′-O(W3)′	2.96		
O(W3)′-O(W4)′	2.93		
Mean	2.98		
	S(1)	Tetrahedron	
S(1)-O(5)	1.502(5)	O(5)-S(1)-O(6)	108.3(3)
S(1)-O(6)	1.482(6)	O(5)-S(1)-O(7)′	108.4(3)
S(1)-O(7)′	1.495(6)	O(5)-S(1)-O(8)	109.5(4)
S(1)-O(8)	1.457(9)	O(6)-S(1)-O(7)′	109.6(3)
Mean	1.484	O(6)-S(1)-O(8)	108.2(4)
		O(8)-S(1)-O(7)′	112.8(4)
O(5)-O(6)	2.41	Mean	109.5
O(5)-O(7)′	2.42		

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O(5)-O(8)	2.39		
O(6)-O(7)'	2.41		
O(6)-O(8)	2.36		
O(7)'-O(8)	2.46		
Mean	2.41		
	S(2)	Tetrahedron	
S(2)-O(1)	1.502(6)	O(1)-S(2)-O(2)	110.2(3)
S(2)-O(2)	1.491(7)	O(1)-S(2)-O(3)	108.6(3)
S(2)-O(3)	1.488(6)	O(1)-S(2)-O(4)	110.7(3)
S(2)-O(4)	1.386(6)	O(2)-S(2)-O(3)	104.9(4)
Mean	1.467	O(2)-S(2)-O(4)	109.1(3)
		O(3)-S(2)-O(4)	112.8(3)
O(1)-O(2)	2.43	Mean	109.4
O(1)-O(3)	2.43		
O(1)-O(4)	2.37		
O(2)-O(3)	2.35		
O(2)-O(4)	2.33		
O(3)-O(4)	2.39		
Mean	2.38		
	S(1)'	Tetrahedron	
S(1)'-O(5)'	1.444(6)	O(5)'-S(1)'-O(6)'	107.3(4)
S(1)'-O(6)'	1.477(6)	O(5)'-S(1)'-O(7)	107.6(4)
S(1)'-O(7)	1.495(6)	O(5)'-S(1)'-O(8)'	111.8(4)
S(1)'-O(8)'	1.452(6)	O(6)'-S(1)'-O(7)	109.9(4)
Mean	1.467	O(6)'-S(1)'-O(8)'	107.9(4)
		O(7)-S(1)'-O(8)'	112.2(4)
O(5)'-O(6)'	2.36	Mean	109.4
O(5)'-O(7)	2.38		
O(5)'-O(8)'	2.41		
O(6)'-O(7)	2.45		
O(6)'-O(8)'	2.37		
O(7)-O(8)'	2.46		
Mean	2.40		
	S(2)'	Tetrahedron	
S(2)'-O(1)'	1.500(6)	O(1)'-S(2)'-O(2)'	109.1(3)
S(2)'-O(2)'	1.460(7)	O(1)'-S(2)'-O(3)'	107.0(3)
S(2)'-O(3)'	1.476(6)	O(1)'-S(2)'-O(4)'	111.0(3)
S(2)'-O(4)'	1.514(6)	O(2)'-S(2)'-O(3)'	106.0(4)
Mean	1.487	O(2)'-S(2)'-O(4)'	112.1(4)
		O(3)'-S(2)'-O(4)'	111.3(4)
O(1)'-O(2)'	2.42	Mean	109.4
O(1)'-O(3)'	2.40		
O(1)'-O(4)'	2.47		
O(2)'-O(3)'	2.36		
O(2)'-O(4)'	2.49		
O(3)'-O(4)'	2.49		
Mean	2.44		

II. Description of the Structure

The structure of Chaidamuite is illustrated in Fig. 1. In the structure, both of Fe and Zn atoms occupy two crystallographically different positions respectively, and S atom occupies four. Two types of the near-regular Fe octahedra, $[Fe(1)O_5(OH)]$ and $[Fe(2)O_5(OH)]$, consist of five O and one OH. A zigzag chain running parallel to the *b* axis consists of the $[Fe(1)O_5(OH)]$ and $[Fe(2)O_5(OH)]$ octahedra sharing OH corners. Four pairs of octahedral corners on either side of this chain are shared by four crystallographically different S tetrahedra, $[S(1)O_4]$, $[S(2)O_4]$, $[S(1)'O_4]$ and $[S(2)'O_4]$. Two types of the Zn octahedra, $[Zn(1)O_2(H_2O)_4]$ and $[Zn(2)O_2(H_2O)_4]$ consist of two O and four H_2O, which link up with the zigzag chain of Fe octahedra by sharing the corners of S tetrahedra. Within each of four types of S tetrahedra, three corners are shared by Fe or Zn octahedra, the fourth O corner being free. The structure contains an octahedral-tetrahedral chain running parallel to the *b* axis, which consists of zigzag chains of Fe octahedra and S tetrahedra sharing four pairs of the corners of Fe octahedra (Fig. 2). These chains are cross-linked by the isolated Zn octahedra into corrugated sheets parallel to the (100) plane. Adjacent sheets are hydrogen-bonded through water molecules.

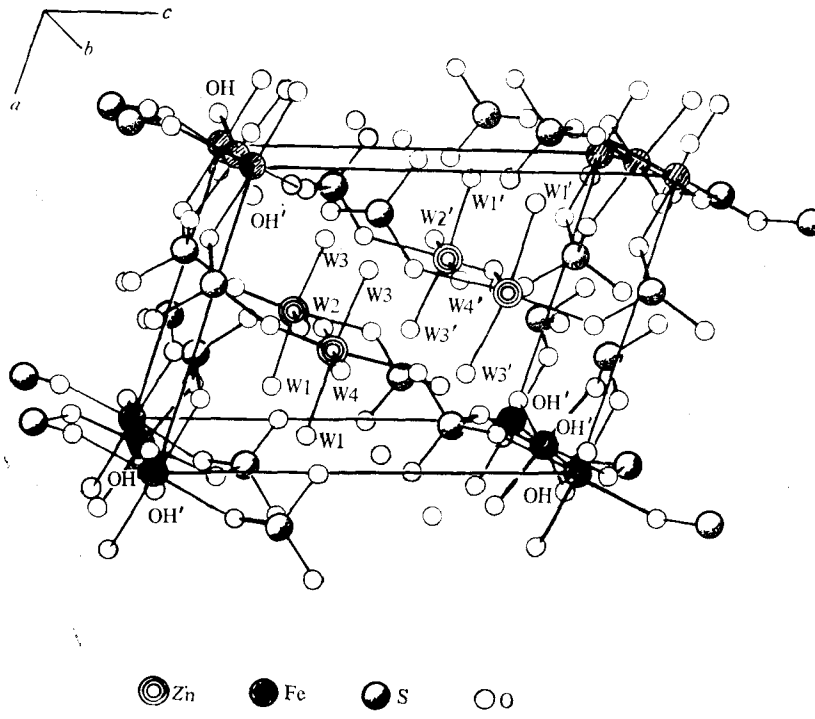

Fig. 1. Crystal structure of Chaidamuite.

The hydrogen bonds formed in the structure are shown in Table 4. The water molecules W(2) and W(3) linked up with water molecules W(3)' and W(4)' belonging to another layer through hydrogen bonds respectively. The water molecule

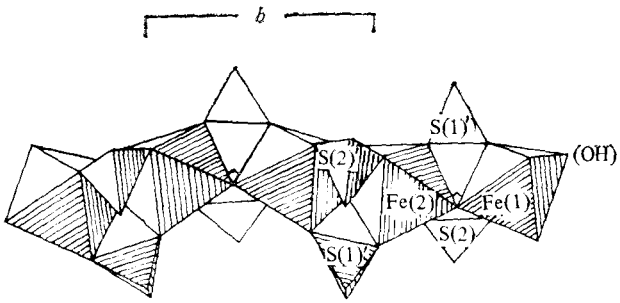

Fig. 2. Octahedral-tetrahedral chain in the structure.

W(3)′ donates one hydrogen bond to one of the bridging corners of the $[S(1)O_4]$ tetrahedron. The water molecules W(2), W(2)′ and W(4) are hydrogen-bonded to the non-bridging corners of the $[S(1)'O_4]$, $[S(2)O_4]$ and $[S(2)'O_4]$ tetrahedron respectively. Besides, in the layer structure, the water molecules W(1) and W(1)′ donate one hydrogen bond to the non-bridging corners of the $[S(1)O_4]$ and $[S(1)'O_4]$ tetrahedron respectively; the water molecule W(3)′ donates one hydrogen bond to the water molecule W(4)′.

Table 4

Hydrogen Bonds in Structure

Atom	Distance (Å)	Hydrogen	Distance (Å)	Atom	Angle (°)
O(W1)	0.965	H(11)	1.896	O(8)	141.3
O(W1)′	0.950	H(11)′	1.917	O(8)′	142.0
O(W3)′	0.950	H(31)′	2.037	O(W2)	145.5
O(W3)	0.905	H(32)	1.974	O(W4)′	170.6
O(W3)′	0.925	H(32)′	2.083	O(6)	133.0
O(W2)	0.950	H(21)	1.824	O(8)′	159.9
O(W2)′	0.950	H(22)′	1.879	O(4)	154.2
O(W4)′	0.956	H(41)′	1.898	O(W3)′	174.3
O(W4)	0.950	H(42)	1.829	O(4)′	129.9

The optical properties correspond to the features of the structure of Chaidamuite. Because of the presence of the octahedral-tetrahedral chains running parallel to the *b* axis in the structure, the absorption of the light is the strongest when the vibration direction of the incident light is along the *b* axis. Therefore, the refractive index of the *b* axis direction of the mineral is the highest ($Ng//b$); the colour of the mineral is also intense.

The corrugated octahedral-tetrahedral layers linking up with the weak hydrogen bond, parallel to the (100) plane in the structure may account for the perfect (100) cleavage of the mineral.

III. Discussion

Chaidamuite has been believed originally to be isostructural with guildite, be-

longing to the monoclinic system, space group $P2_1$[4] because of the similarity in their chemical composition and the pseudosymmetric component in the structure. The determination and refinement of the structure show that the structure of Chaidamuite only belongs to the triclinic system, space group $P\bar{1}$ as a whole.

For this reason, it can be suspected that the real structure of guildite may be also the triclinic system, space group $P\bar{1}$ such as Chaidamuite.

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