Refinement of the crystal structure of krausite: a mineral with an interpolyhedral oxygen–oxygen contact shorter than the hydrogen bond

HERTA EFFENBERGER, FRANZ PERTLIK, AND JOSEF ZEMANN

Institut für Mineralogie und Kristallographie
University of Vienna
A-1010 Vienna, Austria

Abstract

The crystal structure of krausite, $KFe(SO_4)_2 \cdot H_2O$, ($a = 7.920(2)$, $b = 5.146(2)$, $c = 9.014(2)$ Å, $\beta = 102.76(1)°$, space group $P2_1/m$, $Z = 2$) was refined from 614 X-ray data to $R = 0.037$. A previous structure determination was confirmed for the K, Fe, S, and O atoms, and was supplemented by the location of the H atom. In the atomic arrangement an interpolyhedral (= van der Waals) oxygen–oxygen contact of 2.747(2) Å is shorter than the oxygen–oxygen distance of the hydrogen bond with $O\omega$-H . . . O = 2.844(2) Å.

Introduction

The structural parameters of the potassium, iron, sulfur, and oxygen atoms of the monoclinic mineral krausite, $KFe(SO_4)_2 \cdot H_2O$, were determined by Graeber et al. (1965). Recently Zemann (1983) noticed that on the basis of the first investigation the probable hydrogen bond is definitely longer than the shortest interpolyhedral (van der Waals) oxygen–oxygen contact. As this is apparently a novel feature in inorganic stereochemistry and since Graeber et al. (1965) neither located the hydrogen atom nor discussed the probable hydrogen bonds, a refinement of the crystal structure of krausite seemed appropriate.

Working material from Coral Reefs District, Utah, U.S. (Smithsonian Institution, No. 157691) was kindly provided by Pete J. Dunn. To facilitate the comparison with the paper of Graeber et al. (1965) we maintained their orientation of the unit cell and their labeling of atoms.

Experimental and structure refinement

A single crystal chip with the approximate dimensions $0.11 \times 0.15 \times 0.05$ mm was used for the X-ray analysis. The examination of the lattice parameters and the data collection were performed on a Stoe four-circle diffractometer with graphite monochromatized MoKα radiation. The lattice parameters were determined by least-squares techniques from the adjusted angular settings of 29 reflections and are in good agreement with the data given by Graeber et al. (1965). Our values are $a = 7.920(2)$, $b = 5.146(2)$, $c = 9.014(2)$ Å, $\beta = 102.76(1)°$, and $V = 358.3$ Å³ with $Z = 2$. The space group $P2_1/m$ was confirmed by structure refinement.

The intensity measurements were conducted in the $2\theta/\omega$ scan mode with a minimum of 35 steps for each reflection, increased for the (α_1, α_2) splitting (step width 0.05°, step time 0.8 to 1.6 sec per step). In order to test the intensities for radiation damage and/or crystal misalignment, three reference reflections were measured each 60 minutes. A total of 1782 reflections was collected up to $2\theta = 50°$. The quality of our crystal did not allow

measurements further out in reciprocal space. The data were corrected for absorption (linear absorption coefficient $\mu(MoK\alpha) = 31$ cm⁻¹) from empirical ψ scans of three reflections. Additionally, the data were corrected for Lorentz and polarization effects. By averaging symmetry-related reflections a set of 712 unique data was obtained. A subset of 614 reflections with $|F|_o > 2\sigma(|F|_o)$ was used for the structure refinement.

The atomic coordinates given by Graeber et al. (1965) were used as starting values in the full-matrix least-squares refinement. A difference Fourier map revealed the hydrogen atom position. During the final stage of refinement its atomic coordinates and isotropic temperature factor were included in the list of variables. For all the other atoms anisotropic temperature factors were allowed to vary. An isotropic extinction correction was applied (Zachariasen, 1967). Complex scattering factors for neutral atoms from the *International Tables for X-ray Crystallography* (1974) were used. For the 614 reflections with $|F|_o > 2\sigma(|F|_o)$ the final R values are $R = 0.037$ and $R_\omega = 0.025$, where $\omega = 1.331/[\sigma(|F|_o)]^2$. The observed and calculated structure factors are listed in Table 1;[1] Table 2 gives the structure parameters.

Our final atomic coordinates for the potassium, iron, sulfur, and oxygen atoms agree with those given by Graeber et al. (1965) within one e.s.d. The average shift is 0.010 Å, with the largest shift being 0.034 Å for the atom O(2). Because our data set was restricted to relatively small Bragg angles and because the obtained parameters for the temperature factors indicate only moderate and not strongly anisotropic thermal vibrations a detailed discussion of the differences does not seem appropriate.

Discussion

Table 3 presents interatomic distances and bond valences calculated according to Brown and Wu (1976) for our refined structure of krausite. For a projection of the

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Table 2. Structural parameters for krausite

atom	Wyckoff notation	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
K	2(e)	0.5746(2)	1/4	0.2150(2)	1.07(5)	1.93(6)	1.83(6)	0	0.18(4)	0
Fe	2(e)	0.0896(1)	1/4	0.2278(1)	1.24(3)	0.99(4)	1.19(3)	0	0.29(2)	0
S(1)	2(e)	0.6653(2)	1/4	0.6531(2)	1.25(6)	1.01(7)	1.56(7)	0	0.01(6)	0
O(1)	2(e)	0.7399(5)	1/4	0.5191(5)	2.68(21)	1.85(21)	1.79(19)	0	0.46(16)	0
O(2)	2(e)	0.4794(5)	1/4	0.6210(5)	1.14(17)	2.45(23)	3.17(21)	0	-0.25(16)	0
O(3)	4(f)	0.7287(4)	0.0179(5)	0.7499(3)	1.84(13)	1.22(13)	2.09(13)	0.63(11)	0.65(10)	0.38(11)
S(2)	2(e)	0.1554(2)	1/4	0.8817(2)	0.99(6)	0.81(7)	1.18(6)	0	0.31(5)	0
O(4)	2(e)	0.0619(5)	1/4	0.0062(4)	1.78(17)	0.91(18)	1.27(17)	0	0.51(14)	0
O(5)	2(e)	0.3414(5)	1/4	0.9354(5)	0.91(17)	2.54(22)	2.17(18)	0	-0.07(15)	0
O(6)	4(f)	0.1014(4)	0.0167(5)	0.7861(3)	1.72(12)	1.23(13)	1.91(13)	-0.39(10)	0.85(10)	-0.46(11)
O(7)=Oω	2(e)	0.1035(6)	1/4	0.4554(5)	2.80(24)	1.78(26)	1.68(22)	0	0.19(18)	0
H	4(f)	0.145(5)	0.368(8)	0.488(4)	0.70(11)					

E.s.d.'s in parentheses. Anisotropic temperature factors are defined as $\exp[-1/4 \sum_{i=1}^{3} \sum_{j=1}^{3} B_{ij} a_i^{\ast} a_j^{\ast} h_i h_j]$

atomic arrangement parallel to [010] see Graeber et al. (1965).

The main features of the crystal structure as determined by Graeber et al. (1965) have not been changed by our refinement: Krausite contains $[Fe^{[6]}(SO_4)_2 \cdot H_2O]^-$ chains parallel to [010], which are interconnected by potassium ions to form a three-dimensional network. The potassium ions are coordinated by ten oxygen atoms forming a dis-

Table 3. Interatomic distances (Å) for krausite

(a)	cations		s	ligands		
K	-O(1) =2.765(4)		0.17	O(1), O(2)	2x	3.203(4)
K	-O(2) =3.044(2)	2x	0.07	O(2), O(3)	2x b	2.379(4)
K	-O(3) =2.847(3)	2x	0.13	O(2), O(5)'	2x	3.255(6)
K	-O(5) =2.776(4)		0.17	O(3), O(3)	a	2.757(5)
K	-O(5)'=3.049(2)	2x	0.07	O(3), O(5)	2x	3.309(5)
K	-O(6) =2.912(3)	2x	0.11	O(5)',O(6)	2x b	2.395(5)
			$\Sigma=1.10$	O(6), O(6)	a	2.745(5)
Fe	-O(3) =1.971(2)	2x	0.56	O(3), O(3)	a	2.757(5)
Fe	-O(4) =1.961(3)		0.58	O(3), O(4)	2x	2.806(4)
Fe	-O(6) =2.026(2)	2x	0.48	O(3), O(6)	2x	2.897(3)
Fe	-O(7) =2.030(4)		0.47	O(3), O(7)	2x	2.860(5)
			$\Sigma=3.13$	O(4), O(6)	2x	2.852(4)
				O(6), O(6)	a	2.745(5)
				O(6), O(7)	2x	2.774(5)
S(1)-O(1) =1.457(4)			1.58	O(1), O(2)		2.437(6)
S(1)-O(2) =1.436(4)			1.69	O(1), O(3)	2x	2.417(5)
S(1)-O(3) =1.499(2)	2x		1.40	O(2), O(3)	2x b	2.379(5)
			$\Sigma=6.07$	O(3), O(3)		2.389(5)
S(2)-O(4) =1.475(4)			1.50	O(4), O(5)		2.435(6)
S(2)-O(5) =1.445(4)			1.64	O(4), O(6)	2x	2.398(4)
S(2)-O(6) =1.485(2)	2x		1.46	O(5), O(6)	2x b	2.395(5)
			$\Sigma=6.06$	O(6), O(6)		2.401(5)

joined O-O edges of:

    a one [KO$_{10}$] polyhedron and one [FeO$_6$] polyhedron
    b one [KO$_{10}$] polyhedron and one [SO$_4$] group

(b)	oxygen atoms		s			s
O(1)-K	=2.765(4)		0.17	O(4)-Fe =1.961(3)		0.58
O(1)-S(1)=1.457(4)			1.58	O(4)-S(2)=1.474(4)		1.50
O(1)-H	=2.17(4)	2x	0.13			$\Sigma=2.08$
			$\Sigma=2.04$	O(5)-K =2.776(4)		0.17
O(2)-K	=3.044(2)	2x	0.07	O(5)-K' =3.049(2)	2x	0.07
O(2)-S(1)=1.436(4)			1.69	O(5)-S(2)=1.445(4)		1.64
			$\Sigma=1.83$			$\Sigma=1.95$
O(3)-K	=2.847(2)		0.13	O(6)-K =2.912(3)		0.11
O(3)-Fe	=1.971(2)		0.56	O(6)-Fe =2.026(2)		0.48
O(3)-S(1)=1.499(2)			1.40	O(6)-S(2)=1.485(2)		1.46
			$\Sigma=2.09$			$\Sigma=2.05$
	O(7) - Fe =2.030(4)		0.47			
	O(7) - H =0.72(4)	2x				
	O(7)...O(1) =2.844(2)					

E.s.d.'s in parentheses. Bond valences (s) according to BROWN and WU (1976). Only O-O edges < 3.5 Å are given.

torted pentagonal antiprism. All of these oxygen atoms belong to sulfate groups.

During the present work the hydrogen atom was located. Our refinement gave Oω-H = 0.72(4) Å. This value is (as usual in X-ray studies) somewhat short as compared with the results from neutron diffraction structure determinations (Baur, 1970; Chiari and Ferraris, 1982). The H-Oω-H plane of the water molecule is perpendicular to the mirror plane in the space group $P2_1/m$ of krausite. The acceptor atom of the hydrogen bond is the O(1) atom with Oω . . . O(1) = 2.844(2) Å, O(1) . . . H = 2.17(4) Å, and the angle Oω-H . . . O(1) = 155(5)°. Extending the Oω-H distance to 0.97 Å while keeping the Oω-H direction constant would change this angle to 152(4)°. Each water molecule forms two hydrogen bonds to two mirror-related O(1) atoms. The donor and the acceptor oxygen atoms of the hydrogen bond belong to the same $[Fe(SO_4)_2 \cdot H_2O]^-$ chain. The angle H-Oω-H = 115(7)° is somewhat large, but smaller than the O(1) . . . Oω . . . O(1) angle to the

Fig. 1. A $[Fe(SO_4)_2 \cdot H_2O]^-$ chain of krausite in a projection parallel to [$\bar{2}$01]. Hydrogen bonds are drawn with dotted lines and the interpolyhedral (van der Waals) contact O(4)-O(4)' = 2.747(2) Å with broken lines.
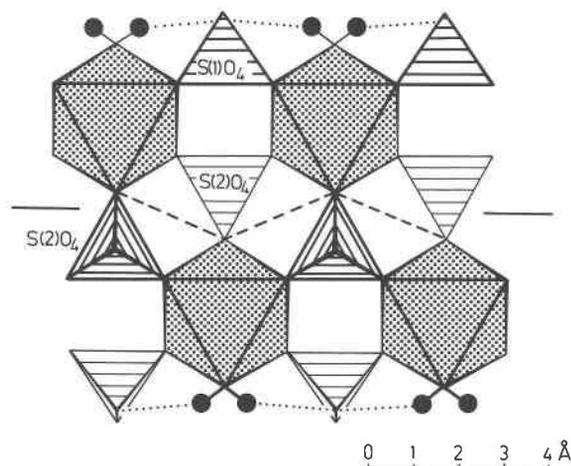
Fig. 2. Theoretical $[Fe(SO_4)_2]^-$ chain with the same topology as that in krausite. The interpolyhedral distance O(4)-O(4)' (broken lines) measures here 3.71 Å.

two acceptor atoms of the hydrogen bond (129.6(2)°). While the plane defined by the Oω atom and the two O(1) atoms that are acceptors of the hydrogen bonds forms an angle of 90.9(3)° with the direction Fe-Oω, the plane H-Oω-H forms an angle of 128(7)° with this direction. As a consequence the angle Fe-Oω-H is 109(3)°, which is equal within the limits of error to an angle of an ideal tetrahedron.

In addition to four neighbors in the $FeO_5(H_2O)$ octahedron and the two O(1) atoms with Oω . . . O(1) = 2.844(2) Å, the Oω atom has two more oxygen atom neighbors at a distance ≤3.20 Å. On the basis of distance alone they could modify the hydrogen bond to a bifurcated or even a trifurcated bond. One of them, an O(1)' atom with Oω-O(1)' = 3.058(6) Å can be immediately discarded from further consideration because the angle at the hydrogen atom, Oω-H . . . O(1)', is only 61(4)°. The other oxygen atom is an O(2) atom with Oω-O(2) = 3.021(8) Å. Because the distance H . . . O(2) measures 2.72(4) Å, while H . . . O(1) measures only 2.17(4) Å (with Oω-H extended to 0.97 Å the corresponding values are 2.65(5) Å and 1.95(5) Å) and because the angle Oω-H-O(1) more nearly approximates 180° than does Oω-H-O(2), O(2) cannot play any important role as an acceptor of a hydrogen bond. The hydrogen bond in all probability goes at least predominantly to the O(1) atom as discussed above.

It is also worth mentioning that there is an O(4)-O(4)' contact of 2.747(2) Å within the $[Fe(SO_4)_2 \cdot H_2O]^-$ chain, which does not represent any edge of the coordination polyhedra round the K, Fe, and S atoms (Fig. 1). Moreover, our structure refinement shows that this O-O contact is definitely not caused by a hydrogen bond. The latter result is in agreement with the bond valence sum of 2.08 v.u. for the O(4) atom (Table 3). Therefore O(4)-O(4)' is an interpolyhedral (i.e., a van der Waals) contact. The $[Fe(SO_4)_2 \cdot H_2O]^-$ chain could easily adopt a geometry in

which such a short interpolyhedral O-O contact is avoided. An obvious example is a geometrically "ideal" $[Fe(SO_4)_2 \cdot H_2O]^-$ chain with the same average Fe-O and S-O bond lengths as in the determined structure, with ideal $FeO_5(H_2O)$ octahedra and SO_4 tetrahedra, and with two faces of the $FeO_5(H_2O)$ octahedron and the O(1)-O(2)-O(2) face of the $S(2)O_4$ tetrahedron parallel to each other (Fig. 2). In this geometrically "ideal" chain all three S(2)-O-Fe angles measure 164.2°, while in the actual structure they measure 134.4° and 144.4° (2x), respectively. The distance O(4)-O(4)' in the "ideal" chain measures 3.71 Å. The probable causes for the distortion of this "ideal" chain (or a similar chain) to the one occurring in krausite, i.e. the one with the somewhat short interpolyhedral O(4)-O(4)' distance, are in our opinion the tendency of the S-O-Fe(III) angles to adopt smaller angles than 164° and/or the constraints imposed on the geometry of the $[Fe(SO_4)_2 \cdot H_2O]^-$ chain by the interconnecting K^+ ions. In this context it should also be mentioned that Zemann (1983) found in the crystal structure of yavapaite, $KFe(SO_4)_2$, (Graeber and Rosenzweig, 1971) similar short O-O contacts at analogous parts within the atomic arrangement. To the best of our knowledge krausite represents the first example of an inorganic structure with an interpolyhedral (van der Waals) oxygen–oxygen contact which is shorter than the hydrogen bond.

The optical constants of krausite (Foshag, 1931) are in qualitative agreement with the atomic arrangement; i.e., the birefringence is positive and very high ($\gamma - \alpha = 0.134$) with the vibration direction of $\gamma = 1.722$ parallel to the $[Fe(SO_4)_2 \cdot H_2O]^-$ chains (cf. Zemann, 1984).

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