

THE CRYSTAL STRUCTURE OF KRAUSITE,
 $\text{KFe}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}^1$

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ABSTRACT

Krausite, $\text{KFe}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$, is an anisodesmic mineral found in the colemanite district of Borate, in the Calico Hills, California. The mineral is monoclinic, $P2_1/m$, $a=7.908$, $b=5.152$, $c=8.988 \text{ \AA}$, $\beta=102^\circ 45'$. Single crystal, counter x -ray intensity data were refined by differential syntheses to $R=0.108$. The crystal structure consists of infinite chains parallel to b of composition $\cdots [\text{Fe}_2(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}]^{2-} \cdots$ linked together by K^+ cations. Each K^+ is coordinated by ten nearest oxygen neighbors at an average distance of 2.92 \AA . In the infinite chains, iron is coordinated to five separate SO_4 tetrahedra and one water molecule. This spacial arrangement of the coordination polyhedra accounts for the perfect (001) and good (100) cleavages in krausite.

INTRODUCTION

The number of hydrated and basic ferric salts whose structures have been determined is relatively small, and among them, ferric sulfates are but sparsely represented. The naturally occurring basic and hydrated sulfates of iron provide a large number of compounds of varied complexity. In many cases these minerals occur in sufficient purity to provide very suitable material for structure determinations. The present investigation is the first of a series of investigations aimed at a systematic study of the ferric sulfate minerals and ferric ion coordination.

Closely related to the alums in composition $[\text{R}'\text{R}''(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}]$, are the lower hydrates of potassium ferric sulfate. None of these have been prepared artificially, but the following occur as minerals: yavapaiite, $\text{KFe}(\text{SO}_4)_2$ (Hutton, 1959), krausite, $\text{KFe}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ (Foshag, 1931), and goldichite, $\text{KFe}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ (Rosenzweig and Gross, 1955). Of these three minerals, krausite is the subject of this report; goldichite and yavapaiite are presently under investigation.

The morphological and chemical investigation of krausite was made by Foshag (1931) on material from the type locality at Borate, Calico Hills, San Bernardino County, California. X -ray data on the unit cell of krausite were reported by Graeber and Rosenzweig (1965).

EXPERIMENTAL WORK

The crystals of krausite used in the present study were from the type

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locality at Borate, California. They consisted of an aggregate of short prismatic crystals less than 1.0 mm in length, closely associated with other sulfates, mostly alunite and coquimbite. Although Foshag reports a varied habit of the monoclinic crystals, the only habit observed by us was that of stubby prisms, {110}, terminated by {001} and $\{\bar{1}12\}$. A brilliant cleavage fragment whose maximum dimension was about 0.4 mm was chosen for single crystal *x*-ray measurements. No attempt was made to grind a sphere of krausite because it exhibits pronounced cleavage. The space group of krausite is established as $P2_1/m$ on the basis of systematic

TABLE 1. CRYSTALLOGRAPHIC DATA FOR KRAUSITE

space group	$P2_1/m$
<i>a</i>	$7.908 \pm 0.010 \text{ \AA}$
<i>b</i>	5.152 ± 0.005
<i>c</i>	8.988 ± 0.010
β	$102^\circ 45' \pm 5'$
cell volume	357.2 \AA^3
cell contents	$2[\text{KFe}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}]$
density, g cm^{-3} , calc.	2.839
obs.	2.840^1
cleavage	(001) perfect ¹ (100) good ¹

¹ Foshag (1931).

extinctions, statistical distribution of observed diffraction intensities, and morphology. The crystallographic data for krausite (Graeber and Rosenzweig, 1965) are listed in Table 1.

An early attempt to solve the structure from two-dimensional projections using visually estimated intensities was unsuccessful (Rimal and Rosenzweig, 1960). Therefore, it appeared more prudent to attempt a three-dimensional approach. The intensities were collected with a G.E. goniostat and diffractometer equipped with a Datex semi-automatic remote controller. Each reflection was recorded in a peak-height fixed-time mode using molybdenum radiation with metal balanced filters (zirconium and yttrium plus aluminum). The response of the scintillation counter was kept linear during all measurements by employing *x*-ray films as attenuators. The counting rate was always below 5000 counts per second. Intensities were measured for 1149 accessible reflections of which 103 were unobserved. The intensities were corrected for Lorentz and polarization factors to obtain the observed structure amplitudes. No corrections for absorption ($\mu R = 0.7$) or extinction were made.

The following atomic scattering factors were used: for potassium, the singly ionized values of Berghuis *et al.* (1955); for iron, the triply ionized

values of Watson and Freeman (1961); for sulfur, the interpolated zero-valence values of Dawson (1960); and for all oxygen atoms, the interpolated values of Berghuis *et al.* (1955).

STRUCTURE DETERMINATION

The unit cell composition requires that potassium, iron and water occupy two-fold special positions. Potassium and iron could occupy positions on symmetry centers, but the only position permissible for water is $2c$ (*i.e.*, in the mirror). The distance between mirrors, $b/2$, is only 2.57 \AA , a space which cannot accommodate more than one oxygen. This situation restricts sulfur to the mirror, *i.e.*, in two sets of special positions $2c$. The symmetry of the sulfate group now requires that two sulfate oxygens also lie on the mirror. The remaining oxygens are necessarily in the 4-fold general position.

A three-dimensional Patterson synthesis with sections normal to the b axis and at intervals of $4/100$ along the three axes was computed on a CDC 1604 computer. A concentration of peaks occurred in the Harker section at height $v = \frac{1}{2}$, in agreement with the assignment of most of the atoms to special positions on spatial considerations. Furthermore, these peaks were spaced about one-half cell apart along the a axis, but did not occur at $u = 0, \frac{1}{2}$ or $w = 0, \frac{1}{2}$. This indicates that the heaviest atoms are probably in the mirror and not on centers. It was assumed that the largest peaks involved Fe and K, and a set of parameters was thus deduced for these atoms. A three-dimensional Fourier calculated at this stage using phases determined from the initial parameters suggested that the position assigned to potassium was more likely occupied by sulfur, and also indicated the position of the remaining set of sulfur atoms and potassium. The suggested positional parameters yielded structure factors with a discrepancy factor

$$R = \frac{\sum ||F_{\text{obs}}| - |F_{\text{calc}}||}{\sum |F_{\text{obs}}|}$$

of 0.43, and the subsequent Fourier synthesis revealed possible positions for the sulfate oxygen atoms and the oxygen atom of the water molecule.

Three cycles of differential syntheses including an assigned isotropic temperature factor ($\exp -B_n \lambda^{-2} \sin^2 \theta$, where B_n is a parameter characteristic of the n th independent atom) for each atom yielded $R = 0.15$. A three-dimensional difference synthesis was calculated which indicated anisotropic thermal motion for several atoms. Anisotropic temperature factors of the form

$$\exp \left(-\frac{1}{4} \sum_{i=1}^3 \sum_{j=1}^3 B_{ij} h_i h_j a_i^* a_j^* \right)$$

were introduced where a_i^* are the lengths of the reciprocal axes, h_i are the Miller indices and B_{ij} are the parameters for the n th atom. These

parameters were refined by several cycles of differential syntheses resulting in a final $R=0.108$.

Table 2 lists the final positional parameters. The average estimated standard deviations (e.s.d.) calculated by the method of Cruickshank (1949) are 0.0008, 0.0018, 0.0014, and 0.0064 Å for Fe, K, and O respectively. Interatomic separations and angles are given in Table 3.

TABLE 2. ATOMIC COORDINATES AND TEMPERATURE FACTOR COEFFICIENTS FOR KRAUSITE

	x	y	z	B ₁₁	B ₂₂	B ₃₃	B ₁₂	B ₁₃	B ₂₃
Fe	0.0892	$\frac{1}{4}$	0.2277	1.201	1.576	0.792		-0.179	
K	0.5742	$\frac{1}{4}$	0.2153	1.407	3.130	1.818		-0.140	
S(1)	0.6655	$\frac{1}{4}$	0.6533	1.273	1.597	1.170		-0.292	
S(2)	0.1555	$\frac{1}{4}$	0.8812	0.917	1.400	0.864		-0.121	
O(1)	0.7401	$\frac{1}{2}$	0.5191	2.800	2.785	1.443		0.224	
O(2)	0.4779	$\frac{1}{4}$	0.6242	1.433	2.445	3.540		-1.208	
O(3)	0.7279	0.0171	0.7494	2.338	2.006	1.832	1.168	0.902	0.906
O(4)	0.0602	$\frac{1}{4}$	0.0057	2.004	2.076	0.592		-0.415	
O(5)	0.3416	$\frac{1}{4}$	0.9363	1.295	3.457	1.660		-0.742	
O(6)	0.1015	0.0154	0.7848	2.108	1.958	1.680	-0.975	1.137	-0.919
O(7)(H ₂ O)	0.1069	$\frac{1}{4}$	0.4563	2.692	2.994	0.986		0.044	

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

Figure 1 is a schematic representation of the structure viewed along the b axis. The coordination polyhedra with cation-anion distances are shown in Fig. 2.

Both SO_4 tetrahedra are significantly distorted as shown in Fig. 2; S(1) has two shorter and one longer and S(2) has one shorter and one longer S-O distances which must be considered significantly different from the average (1.470 Å) of the six independent bond lengths. Similarly, the average of the O-S-O angles deviates only slightly from the ideal value of 109.47°; however, the range (106.5–115.9°) indicates that these groups are significantly distorted. This distortion of the SO_4 tetrahedra may arise from covalency effects since the longest S-O distances of each group are those involving oxygen coordinated to iron. The mean S-O bond lengths of 1.467 and 1.474 Å for the two sulfate groups in krausite compare favorably with the values of 1.472 Å in $\text{Mg}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ and 1.471 Å in $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ (Larson, 1961), and 1.473 Å in $\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$ (Baur, 1964a), 1.471 Å in $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (Baur, 1964c), and 1.474 Å in $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (Baur, 1964b).

The iron atom is coordinated to five separate sulfate-oxygen tetrahedra and one water molecule to form a distorted octahedron (Fig. 2). Inspection of Table 3 shows that this distortion is more complicated than a mere translation of the iron atom along a trigonal axis as the two sets of nearly similar Fe-O bond lengths suggest. Since the ferric ion possesses

TABLE 3. INTERATOMIC LENGTHS AND ANGLES FOR KRAUSITE

Interatomic length		e.s.d.	Interatomic length		e.s.d.
S(1)-O(1)	1.455 Å	0.005 Å	Fe-O(4)	1.958 Å	0.006 Å
S(1)-O(2)	1.448		Fe-O(6')	2.020	
S(1)-O(3)	1.497		Fe-O(7)	2.029	
S(2)-O(6)	1.494		Fe-O(3')	1.974	
S(2)-O(5)	1.446				
S(2)-O(4)	1.481		O(4)-O(6)	2.408	0.008
			O(4)-O(5)	2.440	
K-O(2)	3.025	0.008	O(7)-O(1)	3.075	
K-O(3)	2.835		O(7)-O(2)	2.989	
K-O(6)	2.907		O(7)-O(6)	3.199	
K-O(5)	3.056		O(7)-O(1')	2.834	
K-O(5')	2.764		O(1)-O(2)	2.461	
K-O(1')	2.755		O(1)-O(3)	2.413	
			O(2)-O(3)	2.373	
*O(3)-O(3m)	2.400	0.012	O(6)-O(5)	2.404	
*O(6)-O(6m)	2.418		O(7)-O(7')	3.271	
Bond angle		e.s.d.			
O(1)-S(1)-O(2)		115.89°	0.31°		
O(1)-S(1)-O(3)		109.62			
O(2)-S(1)-O(3)		107.38			
*O(3)-S(1)-O(3m)		106.54			
O(4)-S(2)-O(6)		108.09			
O(4)-S(2)-O(5)		113.01			
*O(6)-S(2)-O(6m)		108.02			
O(6)-S(2)-O(5)		109.74			
O(4)-Fe-O(6')		91.45	0.35		
O(4)-Fe-O(3')		91.41			
*O(6')-Fe-O(6'm)		85.18			
O(6')-Fe-O(7)		86.56			
O(6')-Fe-O(3')		93.13			
O(7)-Fe-O(3')		90.53			
*O(3')-Fe-O(3'm)		88.42			
O(4)-Fe-O(7)		177.29			
*O(6')-Fe-O(3'm)		176.71			
*O(3')-Fe-O(6'm)		176.71			

* Atoms labeled "m" are symmetry related by the mirrors which are normal to the drawing in Fig. 1.

five 3d electrons, one might expect a regular arrangement unless restricted by packing considerations. This appears to be the case in krausite. The average Fe-O distance involving sulfate oxygens is 1.989 Å. This may be compared with the 2.01 Å average (range of 1.89–2.15 Å)

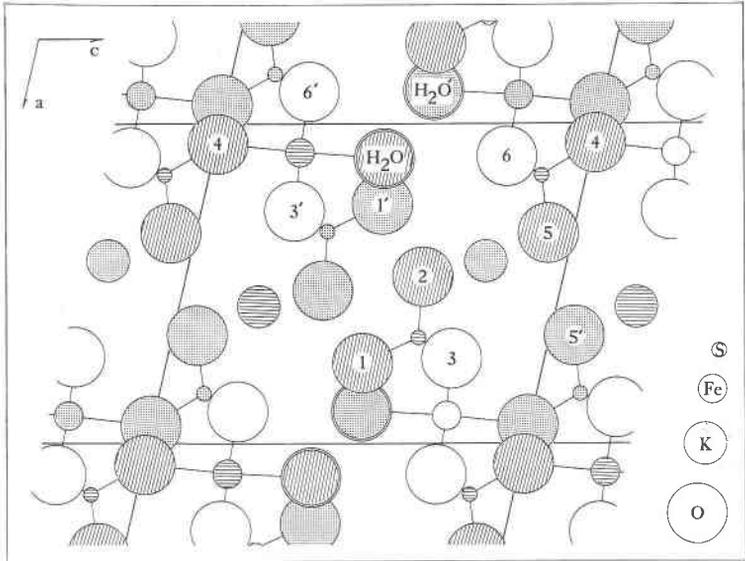


FIG. 1. The structure projected on the ac plane. Atoms lying at $y = \frac{1}{4}$ are hatched; those at $y = -\frac{1}{4}$ ($\frac{3}{4}$) are stippled. Open circles represent superimposed atoms related by mirrors at $y = \frac{1}{4}, \frac{3}{4}$. Symmetry centers are at the origin.

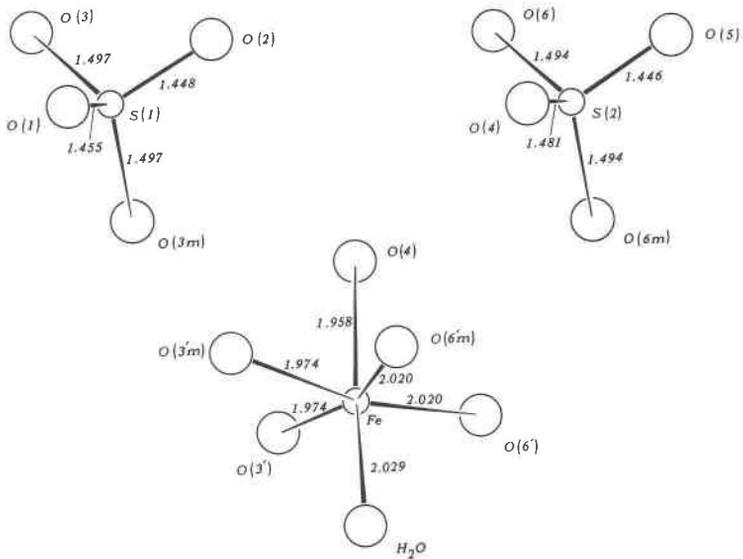


FIG. 2. Coordination polyhedra of sulfur and iron, with bond lengths in angstroms.

ferric-oxygen distance reported in the International Tables (1962). Lacking other ferric-oxygen separations, we may compare those found in krausite with the following ferrous-oxygen (-water) separations: 2.075 Å in $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$ (Morosin and Graeber, 1965), 2.09 Å in $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (Penfold and Grigor, 1959), 2.116 and 2.131 Å in $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (Baur, 1964b), and 2.120 Å found in $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$ (Baur, 1962). As expected, the ferrous-oxygen distances are all greater than the ferric-oxygen distances found in krausite.

The coordination polyhedra of iron and sulfur are joined to form infinite chains parallel to the b axis. These chains have the composition $n[\text{Fe}_2(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}]^{-2}$, and are linked to one another by the potassium ions. Potassium has ten nearest oxygen neighbors at distances ranging

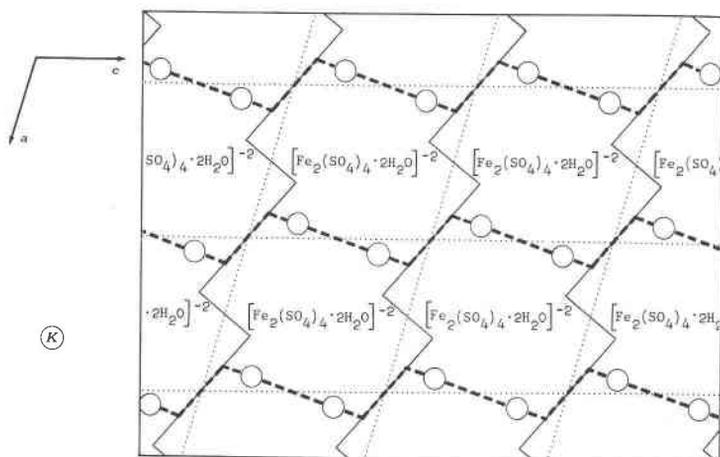


Fig. 3. Relationship of cleavage to the coordination unit $[\text{Fe}_2(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}]^{-2}$ and K^+ . The (100) cleavage is shown by the broken zig-zag line; (001) cleavage by the solid zig-zag line. The origin has been shifted $\frac{1}{2}, 0, \frac{1}{2}$ with respect to Figure 1.

from 2.775 to 3.056 Å. Its position in the structure results in bonding together the $[\text{Fe}_2(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}]^{-2}$ infinite chains; an arrangement which accounts for the perfect (001) and good (100) cleavages in krausite. As shown in Fig. 3, the number of bonds per unit area broken along the c axis is greater than those parallel to the a axis. Due to the spacial arrangement of the coordination polyhedra, there is a pronounced oxygen substructure with these atoms forming roughly hexagonal closest-packed layers parallel to (011).

The anisotropic thermal parameters are reasonably related to the structural packing found in krausite. The potassium thermal parameter, B_{22} , is significantly larger than the other terms (B_{11} and B_{33}), which is in agreement with the longer K-O distances along the b axis. This is true

also with both sulfur atoms in which the longer S-O distances are those associated with the oxygen atoms located across the symmetry plane. In addition, the iron thermal parameter, B_{33} , along the c axis is significantly smaller than the other terms (B_{11} and B_{22}). Unfortunately, no ferric-oxygen separations involving water are available for a critical comparison.

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