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The crystal structure of erdite, $NaFeS_2 \cdot 2H_2O$

JUDITH A. KONNERT AND HOWARD T. EVANS, JR.

U. S. Geological Survey
Reston, Virginia 22092

Abstract

The crystal structure of the new mineral erdite, $NaFeS_2 \cdot 2H_2O$, has been determined from 263 counter-measured intensity data. The mineral is monoclinic, space group $C2/c$, with a = 10.693(1), b = 9.115(1), c = 5.507(4)Å, β = 92.17(2), Z = 4, D (X-ray) = 2.217 g/cm^3. Because of the poor quality of the crystals, the reliability index after anisotropic refinement was not better than 0.170, but the structure is clearly defined. FeS_4 tetrahedra form chains along the c direction by sharing edges. Each Na atom is coordinated to one edge of an FeS_4 tetrahedron, and to four H_2O molecules. The Fe–S bond length is 2.25(1)Å. The $(FeS_2)_n$ chain is very regular and consistent with the dimensions of similar chains previously described in $KFeS_2$, $RbFeS_2$, $CsFeS_2$, and $TlFeS_2$.

Introduction

The new mineral erdite, a sodium thioferrite hydrate, was found in 1976 at Coyote Peak, Humboldt County, California, and described by Czamanske *et al.* (1980). The lustrous copper-colored fibrous crystal masses are disseminated in a dense mafic rock. Careful electron microprobe analyses by G.K. Czamanske indicated the formula to be $NaFeS_2 \cdot xH_2O$. Some variation was found in the water content, which was determined from the mass-total deficiency from 100 percent, but the content was generally consistent with $x \sim 1$. A single-crystal fragment was isolated and mounted for X-ray study by R. C. Erd of the U.S. Geological Survey (for whom the mineral was named), and sent to us for structure analysis.

Our preliminary precession photographs confirmed the crystallography reported by Czamanske *et al.* (1980), but showed a high degree of distortion of the lattice around the c axis, which is the fibrous direction. Reflections of the type $hk0$ were tangentially smeared over several degrees. Prospects for a good structure analysis were therefore discouraging, but an attempt was made, which proved to be successful. The crystal chemistry of the mineral is thus clearly defined in spite of the limits to the degree of refinement imposed by the poor crystal quality. The method of structure analysis and its results are described in this paper.

Crystallography

According to Czamanske *et al.* (1980), erdite is monoclinic and the space group is $C2/c$ or Cc. They report unit-cell parameters refined from power diffraction data to be: a = 10.693(1), b = 9.115(1), c = 5.507(4)Å, β = 92.17(2), V = 536.4Å^3, Z = 4 units of $NaFeS_2 \cdot xH_2O$. These parameters were confirmed by our measurements on the single-crystal diffractometer. The density measured by R. C. Erd is 2.30(1) g/cm^3, but the sample contained minute magnetite crystals. The density calculated for $x = 1$ is 1.99 g/cm^3, and for $x = 2$ is 2.217 g/cm^3.

Experimental procedure and crystal structure analysis

An irregular crystal about 0.3 mm in largest dimension was used for the crystal structure determination. By means of a Picker automatic diffractometer and Nb-filtered Mo$K\alpha$ radiation, intensities were collected for all reflections in the hemisphere with 2θ less than 50°. The crystal was fibrous and the diffraction maxima were broad and irregular, so a scan range of 4° was used. Of the 936 reflections measured, 488 had intensities $>3\sigma(F)$. Lorentz and polarization corrections were made on these observed data, and the reflection pairs hkl and $h\bar{k}l$ were averaged. The final data set consisted of 263 reflections. It was not possible to apply absorption corrections (μ = 35.6 cm^{-1} Mo$K\alpha$).

The structure factors were normalized and found to have a somewhat ambiguous distribution with respect to centrosymmetry. The space group *C*2/*c* was assumed at the start, and the E values were treated by the symbolic addition method (Karle and Karle, 1966). A consistent set of phases was obtained and an E-map was calculated. Because a tetrahedral arrangement of FeS_4 was expected, it was easily recognized that the two strongest peaks on the map represented S and Fe, the latter on the two-fold axis. The third strongest peak, also on the twofold axis, was identified as Na. An electron density map and a difference map were calculated using the Fe and S positions; from these maps the Na position was confirmed and two possible oxygen sites were identified. One cycle of the least-squares analysis was done with only the Fe, S, and Na positions ($R = 0.25$); the Fourier and difference maps calculated at that point showed unequivocally the true oxygen position.

Refinement of this structure in *C*2/*c* with individual isotropic thermal parameters (13 parameters total) converged in three cycles to give a conventional reliability index of 0.183. Three further cycles in anisotropic mode led to $R = 0.170$. The structure so defined was entirely reasonable (and eventually accepted as final), but several further refinement steps were attempted in order to be sure to obtain the best analysis in terms of our limited data set.

We attempted a refinement in space group *Cc*, and in this case, with 23 parameters, convergence was soon reached at $R = 0.150$. The Fe–S chain in the resulting structure became strongly distorted, with Fe–S distances ranging from 2.16 to 2.34Å and isotropic thermal parameters ranging unreasonably from U = 0.003 to 0.059Å^2 for S and O. Anisotropic refinement led to several nonpositive definite thermal parameters. It is clear that the improvement in *R* in this process results chiefly from extreme distortions of the thermal parameters, and does not indicate any advance in the definition of the structure. These results were therefore rejected in favor of the centrosymmetric structure.

Because electron microprobe analysis suggested the presence of considerably less than eight H_2O molecules in the unit cell, we attempted a refinement of the occupancy of the unique site that we found for H_2O. A least-squares analysis in which the occupancy parameter *p* was allowed to vary led directly to a value of $p = 1.10\pm0.13$, that is, full occupancy. A difference map following the last refinement stages showed no unusual features, especially in the region of the H_2O molecule. These observations, in addition to the abnormally low density that a significantly lower water content would predict, unambiguously support a chemical formula of $NaFeS_2 \cdot 2H_2O$ for the erdite crystal that we studied.

The structure was solved and refined (with unit weights) with the aid of computer program XRAY76 (Stewart, 1976). Dispersion corrections were applied using the coefficients of Cromer and Liberman (1970). Scattering factors for Na^+, Fe^{3+}, S, and O were computed from exponential functions using the coefficients of Cromer and Mann (1968).

The final positional and thermal parameters from the anisotropic refinement in space group *C*2/*c* are listed in Table 1. Table 2 lists the observed and calculated structure factors.

Description of the structure

In the schematic view of the erdite structure shown in Figure 1, FeS_4 tetrahedra are seen to form chains along the *c* axis by sharing opposite edges. The tetrahedra are very uniform, and Fe–S distances average 2.25±0.01Å. In the chain, the two S–Fe–S bond angles with the linking S atoms are 104.4±0.4°, and the four lateral angles are 112.1±1.0°. The Na atoms are joined ionically to alternate edges of the tetrahedral chain along opposite sides, forming a complex $(NaFeS_2)_n$ neutral chain. The Na atoms are connected by weak ion-dipole association through the H_2O molecules, so that each Na atom is coordinated in a distorted octahedron to two S atoms at a distance of 2.95±0.03Å and four H_2O molecules at 2.40±0.04Å. In the direction of the *a* axis only van der Waals forces hold these structural elements together. The weak interchain forces account for the soft, fibrous nature of erdite. Individual bond lengths are listed in Table 3.

Ionic Na–S contacts are uncommon, but the distance we found is somewhat longer than three other reported occurrences. One is in Na_2S (antifluorite structure, Zintl *et al.*, 1934), where the Na–S distance is 2.831Å. $Na_2S \cdot 5H_2O$ has an orthorhombic structure in which there is one Na–S bond of 2.87Å (Bedlivy and Preisinger, 1965). In $Na_3SbS_4 \cdot 9H_2O$, the distance is 2.91Å (Grund and Preisinger, 1950). In erdite, the S–Na–S bond angle is 78.5±0.9°.

Figure 2 shows a stereoscopic view of the erdite structure, in which the anisotropic thermal vibrations of the atoms are represented as 50 percent probability ellipsoids. The ellipticities and their orientations

Table 1. Structure and temperature parameters for erdite

Atom	Site	x	y	z	u, Å	
Na	4(e)	0.0	0.387(3)	0.25	0.18(9)	
Fe	4(e)	0.0	-0.001(1)	0.25	0.11(4)	
S	8(f)	0.118(1)	0.864(1)	0.008(2)	0.13(4)	
O (H_2O)	8(f)	0.130(4)	0.584(4)	0.414(6)	0.18(10)	
	U_{11}, Å^2	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Na	0.042(19)	0.036(19)	0.017(17)	0.0	0.007(12)	0.0
Fe	0.021(5)	0.011(5)	0.007(4)	0.0	0.002(3)	0.0
S	0.019(6)	0.022(7)	0.010(6)	0.009(5)	-0.007(4)	-0.001(5)
O	0.065(27)	0.027(20)	0.004(16)	-0.012(18)	0.001(15)	0.005(14)

are generally consistent with the bonding forces imposed on the atoms.

Although microprobe analysis (Czamanske *et al.*, 1980) suggests the presence of one H_2O molecule in the formula for erdite, our study shows conclusively that the crystal we measured contains a full complement of two molecules. Because a difference of one molecule of water would result in a large volume change (if not a major structural change) in the unit cell, it follows that the material used for the crystallographic study of Czamanske *et al.* also was a dihydrate.

Table 2. Observed and calculated structure factors for erdite

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
2	0	0	171	132	6	6	1	40	35	3	5	2	56	47
6	0	0	60	72	10	6	1	34	32	5	5	2	59	56
8	0	0	128	125	-7	5	1	36	30	7	5	2	66	65
10	0	0	50	59	-5	5	1	36	22	9	5	2	47	41
1	1	0	94	84	-3	5	1	43	54	-10	4	2	34	35
3	1	0	65	46	-1	5	1	37	61	-8	4	2	50	66
7	1	0	44	47	3	5	1	57	45	-4	4	2	35	20
9	1	0	59	56	5	5	1	35	40	-2	4	2	33	40
0	2	0	151	105	7	5	1	59	47	0	4	2	103	115
2	2	0	94	84	11	5	1	39	27	2	4	2	48	52
4	2	0	72	71	-8	4	1	34	12	4	4	2	39	26
6	2	0	67	70	8	4	1	32	11	6	4	2	40	21
8	2	0	54	47	-5	3	1	34	21	8	4	2	72	74
10	2	0	33	26	-3	3	1	27	49	-11	3	2	42	27
12	2	0	34	27	3	3	1	31	23	-9	3	2	65	71
1	3	0	42	42	7	3	1	36	22	-7	3	2	66	66
3	3	0	122	130	-10	2	1	39	29	-5	3	2	31	26
5	3	0	91	120	-6	2	1	81	92	-3	3	2	56	52
7	3	0	48	57	-2	2	1	82	90	-1	3	2	134	135
9	3	0	28	9	2	2	1	190	160	1	3	2	118	126
11	3	0	55	39	4	2	1	44	47	3	3	2	37	36
0	4	0	44	48	6	2	1	56	58	5	3	2	30	23
2	4	0	28	41	10	2	1	50	53	7	3	2	75	75
4	4	0	93	117	-3	1	1	67	73	9	3	2	69	72
6	4	0	56	48	-1	1	1	72	48	-8	2	2	53	49
8	4	0	49	16	1	1	1	50	28	-6	2	2	41	45
1	5	0	71	86	5	1	1	41	42	-4	2	2	48	64
3	5	0	82	82	7	1	1	55	42	-2	2	2	94	99
5	5	0	70	74	-2	10	2	44	43	0	2	2	90	84
7	5	0	40	47	0	10	2	51	52	2	2	2	65	62
11	5	0	38	36	1	9	2	47	26	4	2	2	53	65
0	6	0	51	51	-6	8	2	47	48	6	2	2	58	57
2	6	0	49	54	-4	8	2	59	74	8	2	2	44	44
4	6	0	36	40	-2	8	2	36	37	-7	1	2	30	34
6	6	0	32	25	0	8	2	33	17	-5	1	2	72	90
8	6	0	43	37	2	8	2	52	54	-3	1	2	41	49
10	6	0	47	37	4	8	2	64	71	1	1	2	62	53
1	7	0	92	93	6	8	2	39	35	3	1	2	81	93
7	7	0	52	55	-5	7	2	58	65	5	1	2	52	57
9	7	0	56	57	-3	7	2	66	72	11	1	2	36	34
0	8	0	89	84	3	7	2	62	68	-12	0	2	49	54
2	8	0	47	55	5	7	2	64	77	-6	0	2	69	78
4	8	0	39	18	-8	6	2	40	20	-4	0	2	129	174
6	8	0	29	33	-6	6	2	44	56	-2	0	2	157	132
8	8	0	65	56	-4	6	2	49	53	2	0	2	76	75
3	9	0	33	22	0	6	2	37	33	4	0	2	157	165
5	9	0	42	26	2	6	2	49	58	6	0	2	96	95
4	10	0	36	48	4	6	2	43	51	10	0	2	34	21
-5	9	1	34	24	6	6	2	38	34	-3	9	3	34	21
-1	9	1	49	32	-9	5	2	44	52	3	9	3	46	27
-8	8	1	35	13	-7	5	2	42	53	-5	7	3	34	14
0	8	1	33	3	-5	5	2	39	41	3	7	3	37	12
-6	6	1	52	49	-3	5	2	73	75	-2	6	3	61	55
-2	6	1	32	37	-1	5	2	100	102	2	6	3	46	34
2	6	1	60	64	1	5	2	75	71	6	6	3	43	44

Comparison with other Fe–S single-chain structures

The arrangement of $(FeS_2)_n$ tetrahedral chains in erdite is similar to that found in $KFeS_2$ (Boon and MacGillavry, 1942), $RbFeS_2$ and $CsFeS_2$ (Bronger, 1968) and $TlFeS_2$ (Zabel and Range, 1979). The crystallography and principal structural data for all five structures are compared in Table 3.

In the isostructural crystals $KFeS_2$ and $RbFeS_2$, in the absence of water, the cations complete their coordination spheres of eight by further cation–sulfur bonds, creating a three-dimensional network of cation polyhedra with the Fe–S tetrahedral chains forming columns through it parallel to the monoclinic *c* axis. In Figure 3, *c*-axis projections of $NaFeS_2 \cdot 2H_2O$ and $KFeS_2$ are shown for comparison. $CsFeS_2$ and $TlFeS_2$ also contain chains of FeS_4 tetrahedra, but

Table 2. (continued)

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
-9	5	3	37	1	-3	5	4	63	61	7	1	4	52	59
-7	5	3	46	32	-1	5	4	34	26	9	1	4	44	45
-3	5	3	42	24	1	5	4	56	48	-10	0	4	44	48
-1	5	3	36	23	3	5	4	76	79	-8	0	4	68	69
1	5	3	48	39	5	5	4	41	51	-6	0	4	54	47
3	5	3	49	47	-6	4	4	42	37	-2	0	4	71	72
5	5	3	35	20	-4	4	4	65	66	0	0	4	131	121
7	5	3	35	33	-2	4	4	40	28	2	0	4	83	84
0	4	3	41	31	0	4	4	38	10	6	0	4	37	37
4	4	3	32	7	2	4	4	43	31	8	0	4	72	83
-7	3	3	45	40	4	4	4	80	75	2	6	5	46	40
-3	3	3	31	29	-9	3	4	34	9	-5	5	5	52	31
1	3	3	67	65	-7	3	4	40	37	5	3	5	36	37
-6	2	3	36	25	-5	3	4	89	85	7	3	5	43	20
-2	2	3	93	84	-3	3	4	76	72	-8	2	5	37	22
0	2	3	42	42	1	3	4	41	33	-6	2	5	55	32
2	2	3	46	44	3	3	4	94	89	2	2	5	47	43
6	2	3	67	71	5	3	4	70	78	-3	1	5	46	48
-11	1	3	39	19	-8	2	4	35	29	3	1	5	39	13
-7	1	3	50	47	-6	2	4	56	52	7	1	5	56	30
-5	1	3	37	22	-4	2	4	73	63	0	4	6	46	53
-3	1	3	49	36	-2	2	4	55	44	-1	3	6	67	71
1	1	3	65	70	0	2	4	51	42	1	3	6	58	55
5	1	3	34	39	2	2	4	63	64	-4	2	6	37	26
11	1	3	37	27	4	2	4	62	60	-2	2	6	45	36
0	8	4	69	70	6	2	4	42	37	0	2	6	50	50
-1	7	4	52	55	-9	1	4	48	51	2	2	6	51	55
1	7	4	54	58	-7	1	4	33	39	-5	1	6	45	51
-6	6	4	49	13	-5	1	4	32	8	3	1	6	43	60
-2	6	4	43	53	-3	1	4	42	24	-4	0	6	46	63
0	6	4	52	61	-1	1	4	114	94	2	0	6	45	55
-7	5	4	47	33	1	1	4	62	58	4	0	6	59	70
-5	5	4	62	71	5	1	4	33	14*					

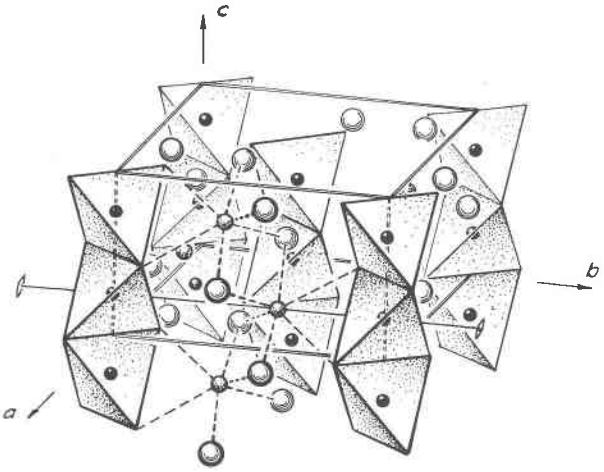

Fig. 1. A pictorial view of the erdite structure. The $(FeS_2)_n$ chains are shown as edge-shared tetrahedra. Large spheres are H_2O molecules, small stipple-shaded spheres are Na atoms. One twofold axis is indicated.

these are cross-linked differently in order to accommodate cations of different size and type.

The structure of $TlFeS_2$ was analyzed recently by a modern least-squares treatment of counter-measured data, while the structures of $RbFeS_2$ and $CsFeS_2$ are based on an electron density–structure factor procedure using data estimated from two or three Weissenberg photographs taken around the needle axis of the crystals. For $CsFeS_2$ (space group *Immm*) a variable *z* parameter must be determined for Fe, which sensitively determines the degree of distortion of the FeS_4 tetrahedron. Bronger (1968) claimed to have proved (but without any error analysis) that the Fe atom is significantly displaced from the center of the tetrahedron, so that Fe–Fe distances along the chain axis would be alternately 2.62 and 2.80Å, and Fe–S bonds would vary from 2.18 to 2.28Å. In order to obtain an internal estimate of the errors inherent in Bronger's data for $CsFeS_2$, we subjected the *F* data

Table 3. Comparison of crystallography of erdite and other $MFeS_2$ structures

	Erdite $NaFeS_2.2H_2O$	$KFeS_2$ (a)	$RbFeS_2$ (b)	$CsFeS_2$ (b)	$TlFeS_2$ (c)
Space group	C2/c	C2/c	C2/c	Immm	C2/c
Unit cell					
a, Å	10.693(1)	7.080(1)	7.22	7.13	11.644(6)
b, Å	9.115(1)	11.310(2)	11.70	11.92	5.308(2)
c, Å	5.507(4)	5.399(1)	5.42	5.42	10.509(5)
β, deg.	92.17(2)	113.22(1)	112.0	-	144.58
V, Å^3	536.4	396.5	424.5	460.6	376.4
Z	4	4	4	4	4
Density (g/cm^3)					
D(x-ray)	2.216	2.665	3.21	3.65	5.722
D(meas.)	2.30	2.61	3.14	3.61	5.66
Bond lengths (Å)					
Fe-S	2.24(1)×2 2.25(1)×2	2.238(1)×2 2.238(1)×2	2.21(4)×2 2.21(4)×2	2.21(9)×2 2.23(9)×2	2.22(5)×2 2.23(5)×2
Avg.	2.246	2.238	2.21	2.22	2.23
Fe-Fe	2.75(1)	2.7006(5)	2.71(2)	2.71(7)	2.654(5)
M-S	2.95(3)×2	3.306(1)×2 3.346(1)×2 3.428(1)×2 3.476(1)×2	3.50(5)×2 3.49(3)×2 3.49(3)×2 3.54(2)×2	3.45(2)×2 3.58(1)×2 3.85(2)×4	3.09(5) 3.24(5) 3.28(5)×2 3.49(5)×2 3.73(5) 3.76(5)×2
Avg.	2.95	3.389	3.48	3.68	3.46
Na-H_2O	2.42(4)×2 2.37(4)×2				
Avg.	2.40				
Reliability index R	0.170		0.121	0.166	0.119

(a) Data from Stevens (1979).
(b) Data from Bronger (1968); structure data recalculated.
(c) Data from Zabel and Range (1979).

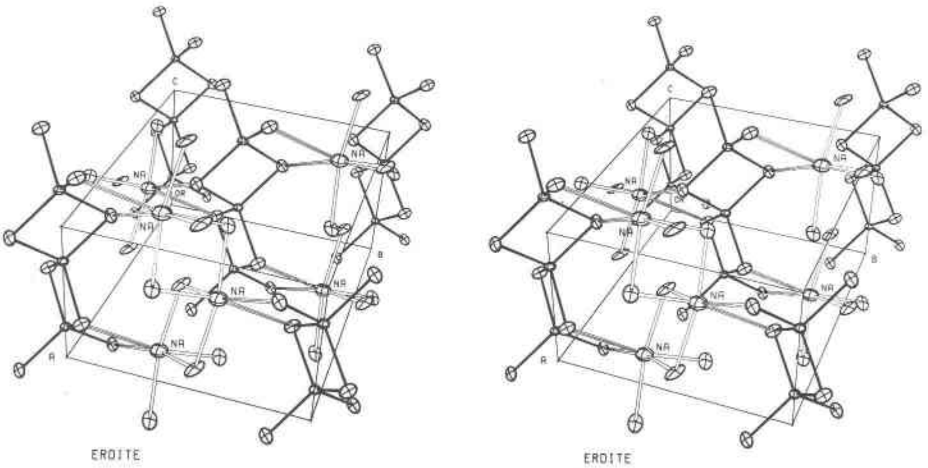

Fig. 2. A stereoscopic view of erdite, in which the thermal motions of the atoms are shown as 50 percent probability ellipsoids. The orientation is similar to that of Fig. 1.

listed in his report to a least-squares analysis. Separate scale factors were assigned to each of the three Weissenberg levels *hk*0 (35 data), *hk*1 (29 data), and *hk*2 (27 data). Although Bronger had carefully interscaled these levels by means of intersecting precession patterns, large adjustment of these factors resulted in a drop in *R* from 0.34 to 0.19. Further refinement of three scale factors, four structure parameters, and four isotropic thermal parameters led to $R = 0.166$. The *z* parameter for Fe, which Bronger determined as 0.242, came to 0.234±0.013 (±0.07Å) in our analysis; that is, not significantly different from 0.25. With this parameter held fixed at 0.250 the value of *R* remained unchanged. The *x* and *y* parameters for the other atoms were not significantly changed from Bronger's values in our treatment.

In $RbFeS_2$ the *z* parameter for Fe is fixed, but is variable for S. We also subjected Bronger's *F* values for this crystal (40 *hk*0 data, 30 *hk*1 data) to a least-squares analysis. With two scale factors, five structure and three thermal parameters, *R* was reduced from 0.155 to 0.12. Again Bronger's *x* and *y* parameters were not significantly changed, but the uncertainty of the S position along the *z* axis is ±0.05Å.

The structure of $KFeS_2$ has recently been reinvestigated with high accuracy by Stevens (1979). This determination now provides the most precise determination of the dimensions of the $(FeS_2)_n$ chain, in which the Fe–S bond length is found to be 2.238±0.001Å.

We have not attempted to rework the structure of $TlFeS_2$.

All published data for these compounds are summarized in Table 3. There is no evidence for any significant distortion from D_{2d} symmetry in the FeS_4 tetrahedron, nor any tendency for the formation of close Fe–Fe pairs along the chain. The Fe–Fe distance varies from 2.65 to 2.75Å among the different structures, apparently in response to the packing requirements of the interchain material. None of the structures reported in this group reveal any Fe–S bond length that is significantly different from 2.238Å found in $KFeS_2$ by Stevens (1979). Stevens has studied the charge-density distributions in this compound in detail by X-ray diffraction, in an attempt to understand better the high one-dimensional electrical conductivity that is characteristic of the $MFeS_2$ compounds. Hoggins and Steinfink (1976) have developed empirical bonding relationships for these compounds, with special regard to Fe–Fe interactions, which are considered to have an important influence on their electrical properties.

Previous syntheses of erdite

The earliest clearly defined synthesis of the compound $NaFeS_2 \cdot 2H_2O$ was described by Schneider (1869). He obtained an anhydrous phase, presumably $NaFeS_2$, by melting together one part (by weight) Fe powder, six parts Na_2CO_3, and six parts S. When leached with water the resulting solid consisted of fine, copper-red needles. After drying over H_2SO_4, chemical analysis indicated a composition close to $NaFeS_2 \cdot 2H_2O$. In a preliminary attempt to reproduce this procedure we obtained a product closely resembling Schneider's description. The X-ray powder photograph showed clearly the erdite pattern, though with lines broadened by poor crystallinity resulting from the low-temperature conversion of anhydrous

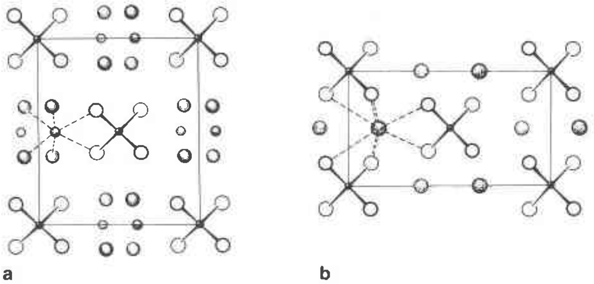

Fig. 3. Plan views along the *c* axis of (a) erdite and (b) $KFeS_2$ (the b axis is horizontal). The x-shaped groups represent the end views of the $(FeS_2)_n$ chains; the alkali atoms are stipple-shaded, surrounded in erdite by H_2O molecules.

$NaFeS_2$ to the dihydrate. (Maghemite and pyrrhotite were present as impurities.)

Thugutt (1892) later prepared $NaFeS_2 \cdot 2H_2O$ directly from aqueous solution, by heating a solution of NaOH saturated with H_2S with iron oxide hydrate for several days. Chemical analysis agreed closely with the dihydrate formula. Thugutt suggested that $NaFeS_2$ may occur in nature, especially in rocks containing nosean or hauyne, which contain the sodium sulfide component. He cites Vogelsang (1874, p. 20) as having observed at high magnification within internal seams in dark brown nosean crystals sparkling metallic needles resembling the thioferrite compounds.

It seems likely that the sodium thioferrite was first formed in the anhydrous state ($NaFeS_2$) in the Coyote Peak matrix, then subsequently transformed to the dihydrate in response to increasing fugacity of H_2O in the late pegmatitic segregations which contain such hydrous phases as phlogopite, natrolite, sodalite, and vishnevite. The anhydrous compound has not been adequately described as a pure phase, either physically or crystallographically. In any case, erdite as described by Czamanske *et al.* (1980) should be regarded as sodium thioferrate dihydrate $NaFeS_2 \cdot 2H_2O$, in accordance with their crystallographic studies, our crystal structure determination, and all previous synthetic studies.

Note added in proof

A recent paper which escaped our attention, published by P. Taylor and D. W. Shoesmith (*Can. J. Chem., 56,* 2797–2802, 1978), describes the green solid products obtained by reaction of solutions of ferric nitrate and sodium hydroxide. Analysis of the green-black product indicated the formula $NaFeS_2 \cdot 2H_2O$, but the water is removed at 100°C by continuous pumping. Their observation that the X-ray patterns are unchanged by dehydration at 100° or 450°C, the authors now believe, results from rapid rehydration of the heated samples on exposure to humidity in the air (personal communication).

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