PISANITE FROM FLIN FLON, MANITOBA[1]

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ABSTRACT

An occurrence of blue zincian pisanite is described from Flin Flon, Manitoba. *X*-ray measurements give a monoclinic lattice, space group $P2_1/c$ with $a=14.12$, $b=6.54$, $c=10.81$A, $\beta=106°$. The unit cell contains 4 [(Fe, Cu, Zn)$SO_4 \cdot 7H_2O$] with Fe:Cu:Zn = 100:80:3 and specific gravity 1.95 (calculated). *X*-ray measurements of a crystal of pure artificial $FeSO_4 \cdot 7H_2O$ gave lattice dimensions $a=14.11$, $b=6.51$, $c=11.02$A, $\beta=105°15'$ with space group $P2_1/c$. The *x*-ray powder patterns of the two materials are almost identical.

During the summer of 1950, several specimens of a bright blue translucent mineral were sent to Professor Bruce Rose of Queen's University by Mr. Ken Rose, from the Cuprus mine about twelve miles east of Flin Flon, Manitoba The mineral occurs as a coarsely crystalline crust up to one quarter of an inch thick on iron, copper and zinc sulphide ores beneath the overburden and also in vugs within the ore and near the bedrock surface. The colour of the mineral is a somewhat lighter shade of blue than that of bluestone (chalcanthite $CuSO_4 \cdot 5H_2O$).

A study of the material by *x*-ray methods soon identified it as a member of the melanterite group of minerals. The data obtained did not, however, agree completely with the published data collected in the recent works of reference (Winchell, 1951 and Dana, 1951). There are inconsistencies in the published data; Wyckoff (1951) quotes two sets of cell dimensions and concludes with the statement: "Evidently more work is needed." It is the purpose of this paper to present the new data and to compare it with that already published.

Crystallography

The mineral occurs as a crystalline crust without development of single crystals. The perfect (001) and poor (110) cleavaged (in the crystallographic setting used in Dana) are easily visible in crushed material and a cleavage fragment suitable for *x*-ray study is readily found.

A cleavage fragment was adjusted on the Buerger precession camera with the good cleavage perpendicular to the pinhole. An orientation precession film readily revealed the position of the symmetry plane. The fragment was then readjusted with the mono-clinic symmetry axis parallel to the dial axis of the instrument. Precession films were taken about the *a* axis (parallel to the good cleavage) and the *c* axis. The adjusted crystal was then transferred to the Weissenberg camera and rotation,

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[1] Referred to as cuprian melanterite in the abstract printed in the *Proceedings of the Royal Society of Canada, 1952, vol.* **46**, *p. 152.*

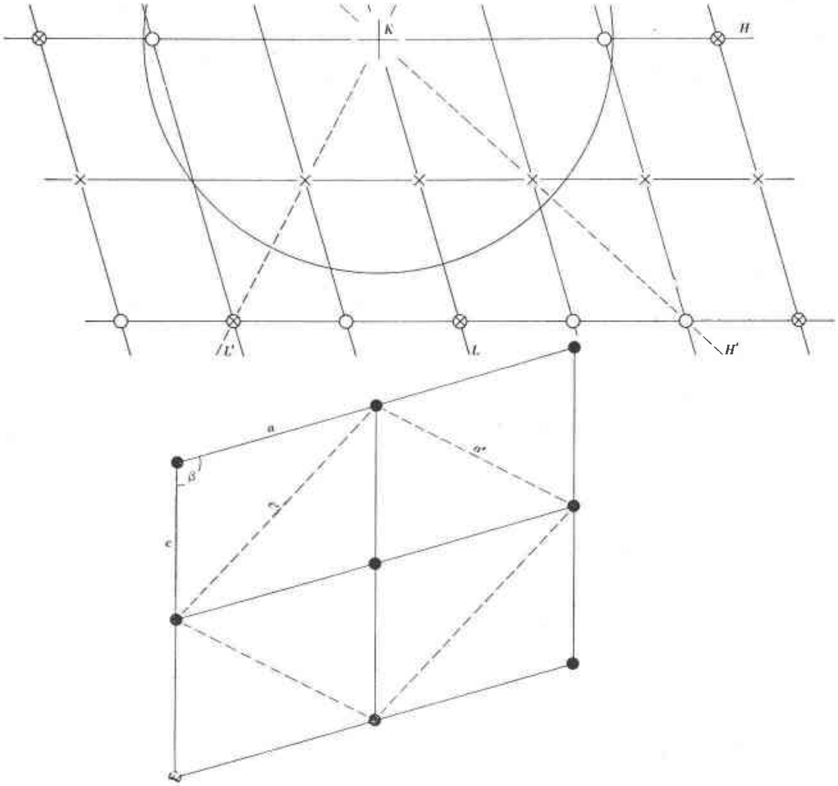

FIG. 1. Reciprocal lattice projection (top) and direct lattice (bottom) of melanterite and pisanite. The cell proposed in this paper is indicated by a, c, β and H, K, L. The B-centred cell of Ness is indicated by a', c', H', K' (the dashed lines). In the reciprocal lattice projection circles represent the observed $h0l$ diffractions and crosses the observed $h1l$ diffractions.

zero and first layer Weissenberg films were taken. Indexing of the precession films and the reciprocal lattice projections of the Weissenberg films (Figure 1) indicated a conventional cell of the monoclinic lattice with the following dimensions:

$$a = 14.12, \quad b = 6.54, \quad c = 10.81\text{A}, \quad \beta = 106°00'.$$

The observed diffractions conform to the following conditions: (hkl) all present, $(h0l)$ present only for $l=2n$, $(0k0)$ present only for $k=2n$. These criteria are characteristic of the space group $C_{2h}^5 - P2_1/c$. In this setting the cleavages are $(\bar{1}01)$ and (111) and the traditional morphological setting of Dana is related to the structural setting by the transformation formula: $10\bar{1}/010/101$.

A small crystal of chemically pure $FeSO_4 \cdot 7H_2O$ was mounted on the precession camera. The films indicated that the crystal lattice is very similar to that for the natural pisanite with space group $P2_1/c$ and lattice dimensions:

$$a = 14.11, \quad b = 6.51, \quad c = 11.02\text{A}, \quad \beta = 105°15'.$$

In Table 1, the lattice dimensions and axial ratios from the literature are listed for comparison with the data obtained here. The early data of Westenbrink (1926) have been accepted by Dana (1951) with the space group given more specifically. Ness (1940) obtained a shorter *b* axis and a different space group, the dimensions are given in the traditional morphological setting. Our data agree closely with those of Ness except for the Herman-Mauguin symbol for the space group. Wyckoff (1951) has given Ness' dimensions in a different setting.

TABLE 1. MELANTERITE AND PISANITE: CRYSTALLOGRAPHIC DATA

	a	*b*	*c*		Space Group	*Z*
Westernbrink (1927)	15.34	12.98	20.02[1]		C_{2h}^6	
Dana (1951)	—	—	—	[104°16′]	C_{2h}^6-F2/d	16
Ness (1940)	15.33	6.50	20.08[1]	[104 16]	C_{2h}^5-P2/c	8
Wyckoff (1951)	15.33	6.50	11.01[1]	118 21		4
Berry ($FeSO_4 \cdot 7H_2O$)	15.45	6.51	20.05A	104 30	$C_{2h}^5-B2_1/x$	8
	14.11	6.51	11.02A	105 15	$C_{2h}^5-P2_1/c$	4
	2.168	1	1.694	105 15		
Melanterite, Dana (1951)	2.1629	1	1.6969	105 30		
Keating & Berry (zincian pisanite)	15.24	6.54	20.01A	105 40	$C_{2h}^5-B2_1/x$	8
	14.12	6.54	10.81A	106 —	$C_{2h}^5-P2_1/c$	4
	2.159	1	1.653	106 —		
Pisanite (Dana, 1951)	2.1789	1	1.6876	106 48		

[1] Probably in kX units.

The morphological axial ratio accepted by Dana (1951), but with *b* halved, fits a *B*-centred cell of the structural lattice. However, there is no symbol for expressing the glide plane in this setting of the space group. The setting adopted here is that chosen by the usual conventions, with *a* and *c* the shortest translations in the symmetry plane and β least obtuse. It is a coincidence that the value for β in the two settings is very similar. Melanterite crystals are most commonly equant in habit and therefore the new setting proposed here would be just as convenient for the geometricl description of the crystals as the morphological setting hitherto accepted.

TABLE 2. MELANTERITE AND PISANITE: *X*-RAY POWDER DATA

Pisanite, Monoclinic, $P2_1/c$, $a=14.12$, $b=6.54$, $c=10.81$A, $\beta=106°$; $Z=4$

$FeSO_4 \cdot 7H_2O$			Pisanite, (Fe, Cu, Zn)$SO_4 \cdot 7H_2O$, Manitoba				
I	θ(Fe)	*d*(meas)	*I*	θ(Fe)	*d*(meas)	*hkl*	*d*(calc)
3	10.3°	5.42A	3	10.4°	5.37A	$\bar{1}11$	5.42A
10	11.5	4.86	10	11.5	4.86	111 $\bar{2}02$	4.88 4.82
1	12.3	4.55	1	12.6	4.44	300	4.52
½	13.4	4.18	½	13.5	4.15	$\bar{1}12$ 012	4.15 4.07
1	14.0	4.00	1	14.0	4.00	211 $\bar{3}02$	4.01 4.00
5	15.0	3.74	5	14.9	3.77	$\bar{3}11$ 310	3.79 3.72
½	15.7	3.58	½	15.4	3.65	112 202	3.68 3.67
½	16.7	3.37	½	16.7	3.37	400	3.39
3	17.5	3.22	3	17.4	3.24	020 311	3.27 3.27
			1	18.0	3.13	$\bar{1}13$ 021	3.15 3.12
1	18.2	3.10					
			1	18.4	3.07	$\bar{2}13$ $\bar{1}21$ 013	3.09 3.09 3.06
1	18.9	2.99	1	18.8	3.01	302 410 121	3.02 3.01 2.99
1	19.5	2.90	½	19.5	2.90	$\bar{2}21$ $\bar{3}13$	2.93 2.88
½	20.5	2.77	½	20.5	2.77	$\bar{1}22$ 022	2.79 2.77
3	20.8	2.73	3	21.0	2.70	411 $\bar{2}22$ 500 $\bar{1}04$	2.72 2.71 2.71 2.69
3	21.6	2.63	3	21.6	2.63	320 122 413	2.65 2.64 2.61

$FeSO_4 \cdot 7H_2O$			Pisanite, Manitoba			$FeSO_4 \cdot 7H_2O$			Pisanite, Manitoba		
I	θ(Fe)	*d*(meas)	I	θ(Fe)	*d*(meas)	I	θ(Fe)	*d*(meas)	I	θ(Fe)	*d*(meas)
1	23.0°	2.48A	—	—	—	½	33.6°	1.750A	1	33.5°	1.755A
½	23.8	2.40	—	—	—	½	34.8	1.697	1	34.7	1.701
2	24.8	2.31	2	24.7°	2.32A	—	—	—	½	35.6	1.664
½	28.0	2.06	1	27.7	2.08	½	36.7	1.621	½	36.4	1.632
—	—	—	1	28.4	2.04	—	—	—	½	37.6	1.588
2	28.9	2.00	2	29.0	1.998	½	38.5	1.556	1	38.2	1.566
2	29.6	1.961	2	29.6	1.961	½	39.3	1.529	—	—	—
½	30.4	1.914	1	30.9	1.886	1	40.2	1.501	1	40.0	1.507
3	31.4	1.859	2	31.6	1.849	½	41.4	1.465	1	45.8	1.351
—	—	—	½	32.6	1.798						

Composition and cell content

A partial analysis of the natural material gave the following atomic proportions of the metal ions present Fe:Cu:Zn = 100:80:3. A spectrographic analysis showed the presence of manganese in minor amount. This composition would lead to the name zincian pisanite as the most appropriate for this mineral. Although melanterite, $FeSO_4 \cdot 7H_2O$, pisanite $(Fe, Cu)SO_4 \cdot 7H_2O$ and boothite $CuSO_4 \cdot 7H_2O$ are isostructural there is no evidence of the existence of a continuous series between the copper and iron members in nature. The primitive cell of the structural lattice contains $4[(Fe, Cu, Zn)SO_4 \cdot 7H_2O]$.

The measured specific gravity 1.91 agrees fairly well with 1.95, calculated for the cell content $4[(Fe, Cu, Zn)SO_4 \cdot 7H_2O]$ with Fe:Cu:Zn = 100:80:3.

X-ray powder pattern

The powder patterns with FeKα-radiation are very similar for pisanite and artificial melanterite. The estimated intensities, (I) and measured spacings (d) are given in Table 2 for both materials together with the indices and calculated interplaner spacings for pisanite. This pattern is diagnostic of the melanterite group but the differences between the two patterns are not sufficiently significant to distinguish between melanterite and pisanite by the *x*-ray powder method.

REFERENCES

DANA, J. D. & E. S. (1951): *System of Mineralogy*, **2**, by C. Palache, H. Berman & C. Frondel, New York.

NESS, I. (1940): Zum Gitterbau des Monoklinen $FeSO_4 \cdot 7H_2O$ (Eisenvitriol, Melanterite), *Naturwiss.*, **28**, 78. (*Min. Abs.*, **8**, 10, 1941).

WESTENBRINK, H. G. K. (1926): The space groups of the rhombic and monoclinic heptahydrates of the sulphates of the bivalent metals, *Proc. Sect. Sci. K, Akad. Wetsnsch. Amsterdam*, **29**, 1223–1232. (*Min. Abs.*, **3**, 345, 1927).

WINCHELL, A. N. & H. (1951): *Elements of Optical Mineralogy*, **2**, New York.

WYCKOFF, R. W. G. (1951): *Crystal Structures*, **2**, New York.