MANGANOAN FERROAN WURTZITE FROM LLALLAGUA, BOLIVIA (I)

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ABSTRACT

"Wurtzite" from Llallagua, Bolivia, is a mixture of polytypes but a $2H$ structure is present which is shown by syntheses and x-ray diffraction to have the composition $(Zn_{0.43}\ Mn_{0.31}\ Fe_{0.26})S$ within about 5 percent uncertainty. This is much lower in zinc than any recorded analyses of wurtzite, but it might be considered to be a ferroan variety of erythrozincite. There are some data which suggest that the ideal composition of erythrozincite is $ZnMnS_2$.

Introduction

During a study of the structure of zinc sulphide minerals by x-ray diffraction methods, we found no examples of $2H$ type wurtzite, although a "wurtzite" from Llallagua, Bolivia, which gave a good $2H$ diffraction, was found to have cell dimensions too large for zinc sulphide (Smith, 1955). Quantitative structural and compositional analyses and syntheses showed that this mineral may belong to the rare species, erythrozincite (Hey, 1950, p. 15).

The material was collected by A. J. Drysdale and is at the University of Toronto under number R595 and at the University of British Columbia under number M2621A79X35. The mineral is black, with a very dark red-brown streak, in hexagonal plates or equant crystals which appear to be a pile of such plates. These crystals partly encrust drusy cassiterite, quartz, and pyrite. The appearance of the assemblage suggests that all of the minerals are of primary hydrothermal origin. In the following report, the structural data and calculations are by Smith, the spectrochemical analysis is by DasGupta, and the syntheses are by Hill.

Arc Spectrochemical Analysis

One small equant crystal of the mineral was detached for quantitative spectrochemical analysis. A small amount of adhering quartz was broken away and a yellow stain was removed with dilute hydrochloric acid before grinding. The first run with no dilution gave lines due to Fe and Mn too intense for quantitative determination. Another run with the mineral diluted 1/12 by weight with pure SiO_2 gave usable intensities. The control spectrographs were made using mixtures of pure Fe_2O_3,

TABLE 1. SPECTROMETRY

Element	Wave Length Å	Weight Percentage of Composite as Oxide
Si	2438.78	(Internal Standard)
Fe	3413.1	13.40
Mn	3070.3	15.55
Zn	3072.1	28.40
Cd	3261.06	0.42
Ag	3382.89	Trace
Pb	2833.07	Trace
Ge	3269.49	Not Detected
Ga	2943.64	Not Detected

Mn_3O_4, ZnO, and CdO with pure SiO_2 in weight concentrations of 10, 3.169, 1, 0.3169, and 0.1 percent. By densitometer readings the apparent weight percentages of Fe, Mn, Zn, and Cd in the mineral were determined. The results are shown below in Table 1. The weight percent numbers of Fe, Mn, Zn, and Cd were converted to weight percentages of the corresponding sulphides, and assuming a composition of (Fe, Mn, Zn, Cd)S, these were recast to total 100, and then to molecular percentages. The results are shown in Table 2.

TABLE 2. CALCULATED COMPOSITION

	Calc. Wt. %		Calc. Mol. %	
FeS	23.8	51.6	25.0	54.4
MnS	27.8		29.4	
ZnS	47.8	48.4	45.2	45.6
CdS	.61		.39	

A qualitative test for sulphur was positive, but the amount of material remaining from the spectrochemical analysis was too small to determine the presence of other anions.

X-Ray Diffraction Analysis

X-ray powder diffraction data on the mineral had been obtained by R. M. Thompson working with the late M. A. Peacock. Two films, one with strong cubic lines, and one with hexagonal lines, were on file. The hexagonal pattern was indexed by Thompson, assuming a two-layer *c*-period. He derived the cell dimensions: $c = 6.32$ Å $a = 3.87$ Å. The indices and spacings of visible lines on the film are shown in Table 3. Precision determinations of the diffraction angle of some of the lines were made recently with a Norelco apparatus, and also are shown in Table 3.

Five preparations of the mineral were made for x-ray diffraction: two were of many small grains, cleaned free from the other minerals by sinking in bromoform, floating in Clerici solution, and briefly digesting in hydrofluoric acid; two were of single hexagonal platy crystals; one was the specimen remaining from the spectrochemical analysis. All were ground in acetone to about 600 mesh, dried, mixed with balsam-xylol solution on a glass plate, dried, cured and ground flat on plate glass.

TABLE 3. X-RAY DIFFRACTION DATA

Powder Camera Data by R. M. Thompson					Spectrometer Measurements (F.G.S.)			
I	θ (Cuα)	d (meas.)	$hk.l$	d (calc.)	I	θ (Cuα_1)	d (meas.)	Remarks
10	13.3	3.35	10.0	3.350	10.0	13.275	3.354	
3	14.1	3.16	00.2	3.155	3.7	14.110	3.160	$2d = c$
5	15.1	2.96	10.1	2.959				
2	19.6	2.30	10.2	2.297				
7	23.45	1.937	11.0	1.935		23.423	1.9377	$2d = a$
5	25.6	1.784	10.3	1.782				
1	27.35	1.678	20.0	1.675				
5	27.85	1.650	11.2	1.649				
1	28.4	1.621	20.1	1.619				
½	31.3	1.484	20.2	1.480				
2	36.0	1.311	20.3	1.311				
1	37.45	1.268	21.0	1.266				
1	38.3	1.244	21.1	1.241				
2	40.7	1.182	21.2	1.175				$kk.l = 10.5$?
1	43.6	1.118	30.0	1.116				
2	45.2	1.086	21.3	1.085				
			30.2	1.052				
1	46.95	1.055	00.6	1.052		46.92	1.0546	$6d = c$
½	49.7	1.011	20.5	1.008				
½	52.7	0.969	22.0	0.968				
3	56.3	0.927	22.2	0.925				$kk.l = 11.6$
2	59.5	0.895	21.5	0.894				
2	64.9	0.851	31.3	0.850				
	$a = 3.87$ Å $c = 6.31$ Å $Z = 2$.					$a = 3.8754 \pm 0.0005$ Å $c = 6.3276 \pm 0.0010$ Å, when $Z = 2$.		

All of the preparations gave a mixture of two diffraction patterns. In the first two, the patterns were of similar intensity, in the second two the hexagonal lines were faint, and in the last the hexagonal lines were very strong. Evidently the two phases found in the earlier work were present in these preparations in different proportions. It was found that the two phases are related to each other as are polytypes of silicon carbide. One has mostly hexagonal packing and larger cell dimensions and the other has a considerable amount of cubic packing but not cubic symmetry.

TABLE 4. UNIT TETRAHEDRAL DIMENSIONS

Prep. No.	Hexagonal Phase			Polytypic Phase		
	a	*c*	*c/a*	*a*	*c*	*c/a*
1	3.874			3.830	3.128	
2	3.875			3.837		
3				3.8364	3.1341	
4				3.8354	3.1334	
5	3.8754	3.1638				
Wt. Mean	3.8754	3.1638	0.8164	3.8358	3.1337	0.8170

The ratio of the two phases in each preparation was evident from the relative intensities of the 11.0 reflections, which are strong in all hexagonal and mixed packing polytypes of this kind, and, in the mixture studied, are separated far enough for full resolution. In the fifth preparation, the ratio of integrated intensities of this reflection gave the ratio of abundance of the hexagonal to the polytype phase to be 6.84.

Knowing the cell dimensions of the two phases, their ratio of abundance, and the composition of the mixture, it is possible to derive the composition of each phase if it can be assumed that (1) both phases are (Zn, Mn, Fe, Cd) S, (2) the ratio of Mn + Fe + Cd to Zn is the only variable affecting the cell dimensions, (3) the ratio of Mn/Fe/Cd is the same in both phases, and (4) the cell dimension variation with composition is linear. Making these assumptions, the molecular percentages in Table 2 were recast; the results are in Table 5. The *a* dimension variation was used to represent composition variation, and the value 3.820 Å given by Swanson & Fuyat (1953) for nearly pure ZnS was used for one end of the series.

The structure of both phases was assumed to be as in hexagonal and polytypic tetrahedral structures based on close-packed lattices. The *a* dimension, which represents the tetrahedral edge dimension, was obtained from the angle of the 11.0 reflection, and the *c* dimension, which represents the tetrahedral height dimension, was obtained from the third order of the basal reflection. The angles of the α_1 lines were read to

TABLE 5. CORRECTED COMPOSITIONS

	Calculated Mol.% Composition of Two Phases			
	Hexagonal Phase		Polytypic Phase	
FeS	27.6	59.6	7.0	15.2
MnS	32.0		8.2	
ZnS	40.0	40.4	84.7	84.8
CdS	.43		.11	

± 0.001° using a very slow scanning speed, and were corrected for instrumental errors by the direct comparison method using a Norelco silicon standard. Angles were found to be reproducible to ± 0.003° for strong spectra and to about ± 0.01° for weak spectra. Diffraction angles were converted to spacings by U.S. Bureau of Standards tables (1950). The a and c (unit layer) values determined in this way are given in Table 4.

If the coordination is tetrahedral, the c/a ratio should be 0.81650 ($\times Z$). The measured ratio for the hexagonal phase is 0.8164 ($\times 2$). Using recent precise data on pure ZnS (Swanson & Fuyat, 1953), and calculating a and c from the spacings of 22.0 and 00.6 respectively, the ratio is 0.8167 ($\times 2$), or apparently also ideal. Therefore the coordination in this mineral is tetrahedral within the limit of measurement.

The structure is apparently wurtzitic with $Z=2$ because the ratio of intensity of 10.0 to 00.2 is between 2 and 3. In the case of other known polytypes this ratio is less than one (Smith, 1955). However, single crystal diffraction study would be necessary to establish the c period (or periods) with certainty.

Synthesis

It is well known that iron, manganese, and cadmium sulphides can be coprecipitated with zinc sulphide from aqueous solution. A general method for increasing the size of the crystals is to heat the precipitate with an alkali halide above the melting temperature of the flux and in a non-oxidizing atmosphere. By this method a few compositions were prepared along the ZnS—$MnFeS_2$ and ZnS—MnS joins, since the data suggested a composition near $Zn(Mn,Fe)S_2$ for the Llallagua mineral. This forms a part of a systematic study of the composition-structure-temperature relations in the ZnS—MnS—FeS system, which will be reported in more detail later; therefore the following data should be considered to be only tentative.

TABLE 6. SYNTHESIS DATA

Exp. No.	Composition Precipitated	Temp. of Crystn.(°C)	Color	Hexagonal Dimensions	
				a (From 11.0 spectrum)	c (From 00.6 spectrum)
H–62	$Zn_{.4}Mn_{.6}S$	787	orange-pink	3.8784	n.d.
H–46	$Zn_{.5}Mn_{.25}Fe_{.25}S$	880	d. red-brown	3.8660	3.157
H–88	$Zn_{.5}Mn_{.5}S$	922	pink	3.8740	n.d.
H–89	$Zn_{.6}Mn_{.4}S$	922	pink	3.8614	n.d.
H–60	$Zn_{.8}Mn_{.2}S$	787	l. pink	3.8418	n.d.
H–90	$Zn_{.9}Mn_{.1}S$	922	l. pink	3.8360	n.d.
H–52	ZnS	986	l. yellow	3.8226	3.122

The precipitates were prepared in a water solution of the combined sulphates, using sodium sulphide in excess. The mixture was kept near 98°C on a water bath for a few days. At first the precipitates containing iron were black, but within a few hours they turned chocolate brown and in a few days were filterable. After washing by decantation, filtering and drying, the material was heated to about 500°C in vacuum to drive off the last of the water. Samples were then mixed with about 10 per cent by weight of alkali chloride, sealed in evacuated pyrex or vycor glass tubes, and heated in a controlled furnace for several days. The crystalline products were ground in water to wash away the alkali chloride, and then were prepared, as described above, for *x*-ray diffraction study.

The critical conditions of the syntheses, and the results, are summarized in Table 6. A plot of the lattice dimension (a) against composition is nearly linear, and the effect of iron and manganese on the dimension is nearly the same. A short extrapolation of the line between the points for ZnS and $Zn_{0.50}Mn_{0.25}Fe_{0.25}S$ passes very near the measured lattice dimension of the Llallagua mineral, at the composition calculated from spectro-chemical data and corrected for a small amount of another phase (Table 5).

The linearity of the above plot is doubtful at high concentrations of MnS, because the a dimension of red MnS(3.976 by Schnaase, 1933; 3.988 by Mehmed & Haraldsen, 1937; 3.9766 in one of our preliminary determinations) is larger than the linear extrapolation of the (Zn,Mn)S points by about 0.065Å. This suggests that the relation is curved. Making a reasonable curve to satisfy the data, the point representing the Llallagua mineral is too low in zinc sulphide by about 2 mol percent, neglecting the small effect of the cadmium sulphide present, or by about 3 mol percent when this is included. Therefore the most probably composition of the mineral is $(Zn_{0.43}Mn_{0.31}Fe_{0.26})S$, with an uncertainty of about 5 percent. However we have no data on the anion composition, other than that sulphur is present. Our data on the relation between lattice dimension and composition of (Zn,Mn)S do not agree with those of Kröger (1939, 1940); therefore the uncertainty of composition of the mineral is somewhat greater than given above until the reason for the discrepancy is determined.

X-ray powder diffraction films of synthetic $(Zn_{0.50}Mn_{0.25}Fe_{0.25})S$ and hexagonal ZnS are shown in Fig. 1 with that of the Llallagua mineral.

Erythrozincite, as first described by Damour (1880), is a red-colored zinc-manganese sulphide with optical properties similar to wurtzite (Des Cloizeaux, 1881). Kröger (1939) synthesized orange-red (Zn,Mn)S, and demonstrated a complete hexagonal series from ZnS to about $(Zn_{0.45}Mn_{0.55})S$ when at equilibrium with green cubic MnS (albandite), at

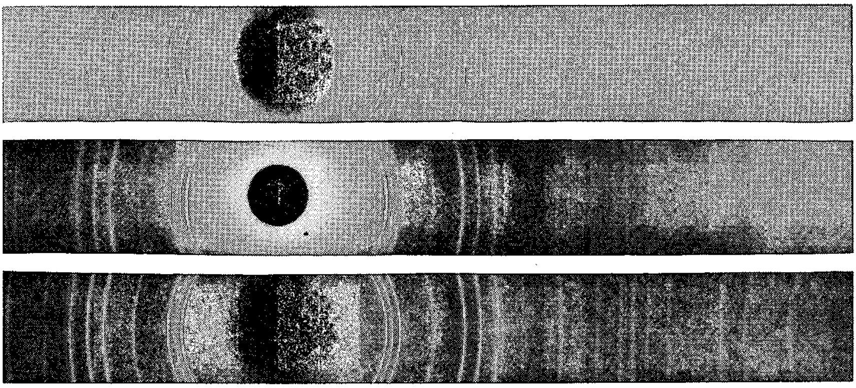

FIG. 1. *X*-ray powder diffractions with Cu$K\alpha$ radiation and camera circumference of 180 mm. (1 mm. on film = 1° θ) *Top*—synthetic Zn_2FeMnS_4 (Exp. H46); *Middle*—manganoan ferroan wurtzite from Llallagua, Bolivia (print of Thompson's film yielding data in table 3, any visible difference in scale with top film is due to different camera used or different treatment of prints); *Lower*—synthetic ZnS (Exp. H52).

1180°C. Kullerud (1953) similarly showed that the composition of brown hexagonal (Zn,Fe)S extends to $(Zn_{0.54}Fe_{0.46})S$ at 1050°C, and to $(Zn_{0.52}Fe_{0.48})S$ at 1170° when at equilibrium with hexagonal FeS (pyrrhotite). We have found that (Zn,Fe)S is chocolate brown, and the color of (Zn,Mn,Fe)S is determined principally by the amount of iron present. We have not established the saturation composition of these phases when at equilibrium with both alabandite and pyrrhotite. However, since the atomic volume of Mn and Fe in the ZnS structure are very nearly the same, and considering the above limiting compositions determined by Kröger and by Kullerud, it would be expected that they would have about the same solubility in ZnS structures.

The composition of the Llallagua mineral and the limiting compositions of synthetic (Zn,Mn)S and (Zn,Fe)S suggests that the Zn and Mn or Fe positions are ordered and that the composition is approximately $Zn(Mn,Fe)S_2$. Unfortunately, the similarity of size and scattering power of the cations makes such a determination difficult. However, there are enough data to justify the hypothesis that the ideal composition of erythrozincite is $ZnMnS_2$.

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