MANGANOAN FERROAN WURTZITE FROM LLALLAGUA, BOLIVIA (II)

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An unusual wurtzite from Llallagua, Bolivia, has been described elsewhere in this number by Smith, DasGupta & Hill. The mineral is represented by an x-ray powder film in the University of Toronto files, which had been satisfactorily indexed as a $2H$ polymorph by Dr. R. M. Thompson. The cell dimensions he derived are distinctly larger than those obtained by various workers on $2H$ wurtzite formed by heating pure sphalerite (Table 1). This difference has been shown by Smith, *et al.* to be due to substantial substitution of Zn by Mn and Fe.

TABLE 1

	Llallagua, Bolivia[1]	heated sphalerite[2]
a	3.87 Å	3.819 Å
c	6.31	6.246

[1]Cell dimensions by R. M. Thompson.
[2]Cell dimensions by M. L. Fuller (1929), converted to Angstrom units.

It seemed desirable to supplement the powder diffraction work of Smith, *et al.* with single crystal studies. This was made possible through the generosity of Professor R. M. Thompson, who provided several fine specimens from the University of British Columbia collections. With this material, morphological measurements and Weissenberg, precession and powder x-ray studies were undertaken.

Two zinc-bearing sulphides are evident in the specimens. One occurs abundantly as massive material, and has the physical properties of iron-bearing sphalerite. Carefully selected cleavage fragments give x-ray powder films which show only the reflections characteristic for this mineral. The second sulphide is present as rough hexagonal plates, measuring up to several millimetres in diameter. The crystals show in addition to the broad basal face, a narrow hexagonal prism, and occasionally a hexagonal pyramid.

Weissenberg films of the hexagonal plates, with the normal to the platy development as rotation axis, show hexagonal symmetry. The systematic extinctions are characteristic of the space group *C6mc*, like ordinary wurtzite, assuming that the crystal class is *6mm*. The cell dimensions

$$a = 3.881, \qquad c = 6.315 \text{ Å},$$

refined by extrapolation of the spacings obtained from an indexed powder film of camera diameter 114.6 mm., are in substantial agreement with those of Thompson, and of Smith, *et al.* But, as pointed out by these authors, the dimensions are notably greater than recorded for ordinary wurtzite.

Two-circle goniometric measurements were not suitable for the calculation of axial ratios, but proved that the hexagonal pyramid has the indices $(10\bar{1}1)$. Several faces gave ρ angles of about $62\frac{1}{2}°$, in satisfactory agreement with the value 61°59′ calculated from the cell dimensions.

It seems that the Llallagua wurtzite is invariably intergrown with sphalerite. Rotation films with [00.1] as rotation axis, show also the [111] period of sphalerite. Precession films with *a*[10.0] as precessing axis, are useful for determining the crystallographic relationships of the intergrowths. Fig. 1 is a reproduction of such a film. The sphalerite reflections are shown as open circles and their positions relative to the wurtzite reflections indicate that three [110] sphalerite axes coincide with the *a* axes of wurtztite. Thus, as one might expect, a (111) plane of sphalerite and the (00.1) plane of wurtzite are so oriented that the rows of greatest atom density in the two planes coincide in direction.

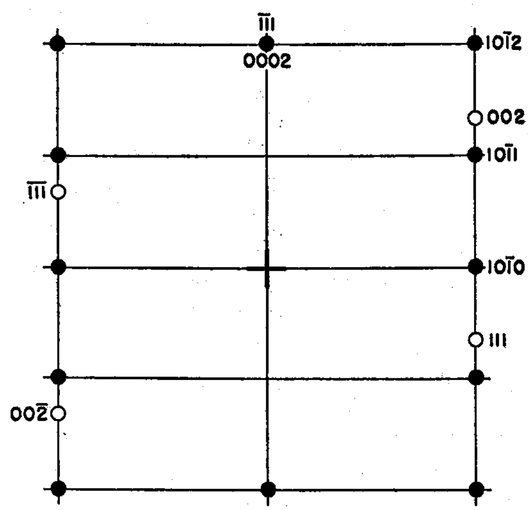

FIG. 1. Reproduction of zero level precession film of a wurtzite crystal, with *a*[10.0] as precessing axis. Open circles represent sphalerite reflections.

Four selected wurtzite crystals, weighing between 18 and 24 mgrs. each, gave specific gravities ranging from 3.64 to 3.73, with the most compact specimen giving the highest value. This compares with 4.10 measured on a cleavage fragment of white sphalerite, and 4.101 calculated for *2H* wurtzite with assumed chemical composition ZnS (Frondel & Palache, 1950). Evidently the specific gravity of the Llallagua wurtzite, free of sphalerite, would be somewhat lower than the highest measured value, 3.73.

Two samples were prepared for *x*-ray spectrographic analysis, with the results given in Table 2. Sample 1 consisted of carefully selected cleavage fragments of sphalerite, which may nevertheless, have contained some wurtzite. The metal content of this material is compatible with the composition of a high-iron sphalerite. Sample 2 consisted of a quantity of the hexagonal platy crystals, weighing in total about 200 mg. The atomic proportions of the metals calculated from this analysis are near Zn:Mn:Fe = $1:\frac{1}{2}:\frac{1}{2}$. The calculated specific gravity for wurtzite

Table 2. *X*-ray Spectrographic Data

	1	2	3
Zn	47.6%	35.4%	1.000
Mn	0.6	13.6	0.46
Fe	11.8	12.3	0.41
Cd	—	0.1	—
	60.0%	61.4%	

1. Weight per cent of metals—selected cleavage fragments of sphalerite. 2. Weight per cent of metals—hexagonal crystals. 3. Atomic proportions calculated from analysis 2, on the basis Zn = 1.00.

with the composition $(Zn_1Mn_{\frac{1}{2}}Fe_{\frac{1}{2}})S_2$, and our cell dimensions, is 3.73. The single crystal *x*-ray studies described above indicate that some sphalerite was contained as an intergrowth in the crystals. Presumably then, the values obtained in the second analysis lie between those for the cleavage fragments of sphalerite and the actual composition of the wurtzite. From this it may be deduced that the total number of Mn and Fe atoms is at least equal to the number of Zn atoms. The analyses have limited quantitative value, for obvious reasons, but the calculations do indicate that the cell dimensions, measured specific gravities and analyses are compatible.

The unusual cell dimensions and specific gravity are in keeping with changes observed in the constants of sphalerite with increasing substitution of Fe for Zn. Allen, Crenshaw & Merwin (1912) observed that the specific gravity decreased from 4.090 with 0.2% FeS to 3.935 with 28.2% FeS. More recently, Chudoba & Mackowsky (1939) have shown that the cell edge increases from 5.423 Å with 0.16% Fe to 5.450 with 26.20% Fe. Similar, but less quantitative results have been recorded for wurtzite. The present study has shown that the substitution of Mn for Zn has a greater effect on the cell dimensions and specific gravity.

Acknowledgment

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References

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