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THE RELATIONSHIP BETWEEN UNIT-CELL EDGES AND COMPOSITION OF SYNTHETIC WURTZITES[1]

BRIAN J. SKINNER AND PHILIP M. BETHKE, *U. S. Geological Survey, Washington 25, D. C.*

ABSTRACT

Synthetic 2H wurtzites have been prepared in the composition planes ZnS-FeS-MnS and ZnS-FeS-CdS. In both planes, the unit-cell edges are linear functions of the composition expressed in mol per cent.

The cell edges of Fe- plus Mn-bearing wurtzites are described by the linear functions

$$a = 3.8230 + 0.000490\ X + 0.001628\ Z$$
$$c = 6.2565 + 0.000886\ X + 0.002089\ Z$$

where a and c are in Ångstrom units and X and Z are the FeS and MnS contents respectively.

The cell edges of Fe- plus Cd-bearing wurtzites are defined by the linear functions

$$a = 3.8230 + 0.000490\ X + 0.003124\ Y$$
$$c = 6.2565 + 0.000886\ X + 0.004555\ Y$$

where a and c are in Ångstrom units and X and Y are the FeS and CdS contents respectively, in mol per cent.

INTRODUCTION

Wurtzite (ZnS) is hexagonal, space group $P6_3mc$, $Z=2$. Like sphalerite, it does not appear to deviate measurably from the stoichiometric formula. It can, however, tolerate very extensive solid solutions, whereby iron, manganese, cadmium and other cations can replace zinc in the structure, and anions such as selenium and oxygen can replace the sulfur. Numerous previous studies have demonstrated that measurable changes in the unit-cell edges of wurtzite accompany the compositional changes of the solid solutions.

Wurtzite is the high temperature polymorph of ZnS, sphalerite being the phase stable at room temperature. Allen and Crenshaw (1912) determined the temperature of the sphalerite-wurtzite transition for pure ZnS as 1020° C. and demonstrated that the transition temperature was lowered by the presence of iron in solid solution. Kullerud (1953) studied the effect of iron, manganese and cadmium on the sphalerite-wurtzite transition, showing that all three caused a significant decrease in the transition temperature.

Frondel and Palache (1950), Strock and Brophy (1955) and others have demonstrated that regular one-dimensional stacking faults may occur in wurtzites, giving rise to higher periodicities along the c-axis than the 2-layer repeat of common, or 2-layer hexagonal (2H) wurtzite. All

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wurtzites prepared in the present study have the basic 2H structure. This statement is based on the x-ray work of D. Appleman, who kindly studied a number of single crystals by the Buerger precession method and found them all to be 2H. In addition, x-ray diffractometer tracings and x-ray powder diffraction films were made of all compounds prepared, and no lines were observed that could be attributed to a stacking sequence other than 2H.

SAMPLE PREPARATION AND MEASUREMENT

All wurtzite samples were prepared by heating mixtures of the requisite amounts of ZnS, FeS, MnS and CdS in sealed, evacuated, silica-glass tubes. The starting compounds were prepared from the same zinc, iron and sulfur described by Skinner *et al.* (1959) and the same manganese and CdS described by Skinner (1961).

Unit-cell edge measurements were all made with the x-ray diffractometer using copper radiation. The (110), (200), (210) and (300) spacings were used to determine a and the (103), (004), (203) and (114) to determine c. NaCl was used as an internal standard of measurement; the unit-cell edge of NaCl was taken from Frondel (1955) and converted from kX to Å by the conversion factor 1.00202 (Bragg, 1947).

Individual diffraction lines were measured by successive oscillations, each oscillation including both the reference line of the internal standard and the wurtzite line under observation. A minimum of six oscillations were made over each line. The samples prepared by Bethke (samples labeled B, Table 5) were measured against NaCl, using the step-scanner attachment on the x-ray diffractometer. Two individual measurements were made for each composition, the sample being rotated 180° about an axis perpendicular to the surface, after each measurement.

A value for a, independent of c, was calculated directly from each measurement of the $h00$ and $hk0$ spacings selected. The calculated a's were combined by taking the average, and the average a used to calculate a value for c from the measured spacings of the (103), (203) and (114) reflections. A value for c, independent of a, can be calculated directly from the (004) spacing. All the calculated c's were averaged to get the value of c quoted for a given composition.

The values quoted in Tables 4–9 for the cell edges of individual compounds are the numerical averages of all measurements of the compound. The precisions stated have no statistical significance and are simply the maximum observed deviation from the numerical average. Previous studies have shown that the methods employed allowed the same reproducibility to be attained by different workers, using different equipment (Skinner *et al.*, 1959).

UNIT-CELL EDGES OF PURE WURTZITE

The cell edges of pure wurtzite have been measured by a number of workers, and these values have been gathered for comparison in Table 1.

It is apparent that there is reasonable agreement between various workers for the value of a. Agreement on the value of c, however, is less satisfactory. Swanson and Fuyat (1953) and the present authors are in essential agreement, but the values of other workers are widely scattered. The reason for these discrepancies cannot readily be found in compositional differences, except perhaps in the case of Ulrich and Zachariasen (1925) who recorded both a and c significantly greater than anyone else. The discrepancies may possibly be found in differences of measurement procedure, but unfortunately most workers did not describe their methods in sufficient detail to allow adequate review. However, Smith *et al.* (1957) specifically state that they used the (110) reflection to determine a and the (006) to determine c. Although (006) is a permissible reflection in the space group $P6_3mc$, it was not observed in powder patterns taken in the present study, nor in the extremely careful and detailed study of Swanson and Fuyat (1953). It is probable that Smith and his co-workers mistook the strong (302) reflection for that of the (006). Recalculating their data on this assumption, a value for c of 6.257 Å is obtained, in good agreement with our results and those of Swanson and Fuyat (1953).

Lacking further details on which to evaluate the other measurements we have used the cell edges of pure wurtzite determined in the present study to construct the curves of cell edge versus composition.

TABLE 1. UNIT-CELL EDGES OF WURTZITE (ZnS)

Investigator	Unit-cell edges	
	a, Å	c, Å
Ulrich and Zachariasen (1925)	3.844[1]	6.290
Fuller (1929)	3.819[1]	6.247
Kroger (1938)	3.819[1]	6.247
Swanson and Fuyat (1953)	3.820[2]	6.260
Kullerud (1953)	3.8217±0.0003[1]	6.2702±0.0003
Smith *et al.* (1957)	3.8226	6.244
Skinner and Barton (1960)	3.8232	Not reported
Skinner and Barton (1960)	3.8237	Not reported
Present study	3.8230±0.0005[3]	6.2565±0.0006

[1] Converted from kX to Å by the kX/Å conversion factor, 1.00202.
[2] At 26° C.
[3] At 25° C.

Table 2. Unit-Cell Edges of Greenockite (CdS)

Investigator	Unit-cell edges	
	a, Å	*c*, Å
Ulrich and Zachariasen (1925)	4.150[1]	6.738
Kroger (1939)	4.139[1]	6.705
Swanson, *et al.* (1955)	4.136[2]	6.713
Smith (1955)	4.1348±0.0015	6.7490±0.0010
Hurlbut (1957)	4.143	6.729
Present study	4.1354±0.0008[2]	6.7120±0.0007

[1] Converted from kX to Å.
[2] At 25° C.

Unit-Cell Edges of Greenockite (CsS)

Greenockite (CdS) has the same structure as wurtzite, but a considerably larger unit cell. The values of $a = 4.1354 \pm 0.0008$ Å and $c = 6.7120 \pm 0.0007$ Å at 25° C. for the cell edges of pure greenockite, recorded in the present study, are in good agreement with the careful study of Swanson *et al.* (1955) (Table 2). The *a* value is also in excellent agreement with the 4.1348 ± 0.0015 Å reported by Smith (1955). Smith's *c* value of 6.7490 ± 0.0010 Å is in poor agreement with the present study, however. As in the case of wurtzite, Smith used the (006) reflection to determine *c*, but since neither Swanson *et al.* (1955) nor the present author recorded the (006) on powder films or diffractometer tracings, it is believed Smith mistook the (302) for the (006). Recalculating his data on this assumption gives a value of 6.724 ± 0.001 Å for *c*, in better agreement with the present study.

Table 3. Unit-Cell Edges of FeS-Bearing Wurtzites Determined by Kullerud (1953). Converted from kX to Å Units and Corrected for Errors in mol Per Cent Calculations

FeS content		Unit-cell edges (corrected)	
Weight per cent	Mol per cent (corrected)	*a*, Å	*c*, Å
0	0	3.8217±0.0003	6.2702±0.0003
4.75	5.24	3.8233±0.0004	6.2733±0.0004
9.30	10.21	3.8243±0.0004	6.2765±0.0004
22.00	23.82	3.8296±0.0004	6.2880±0.0004
30.00	32.20	3.8324±0.0004	6.2943±0.0004

BINARY WURTZITES

Fe-bearing wurtzites

Kullerud (1953) demonstrated that a discontinuous solid-solution series with the wurtzite structure extends from ZnS to approximately 42 mol per cent FeS. He also presented a series of measurements for the cell edges of Fe-bearing wurtzites. His measurements are incorrectly stated as being in Å, whereas they are actually in kX units. Kullerud used NaCl as an internal standard of measurement, taking the unit-cell edge of pure NaCl from Wyckoff (1948). The confusion over units arose from an error by Wyckoff who misquoted the cell edge of NaCl in Å when it should have been in kX. There is also a minor numerical error in Kullerud's conversions of weight per cent to mol per cent. Corrected values of Kullerud's data are presented in Table 3 and Fig. 1. Cell edges of Fe-bearing wurtzites determined in the present study are presented in Table 4 and graphically in Fig. 1. The disagreement between Kullerud's data and the present study is disturbingly large. The curves for *a* versus composition diverge slightly, in the same manner that the *a* versus composition curve for Fe-bearing sphalerites was found to diverge from Kullerud's curve (Skinner *et al.*, 1959). The explanation possibly lies, as suggested for the sphalerite case (Skinner *et al.*, 1959), in the use of

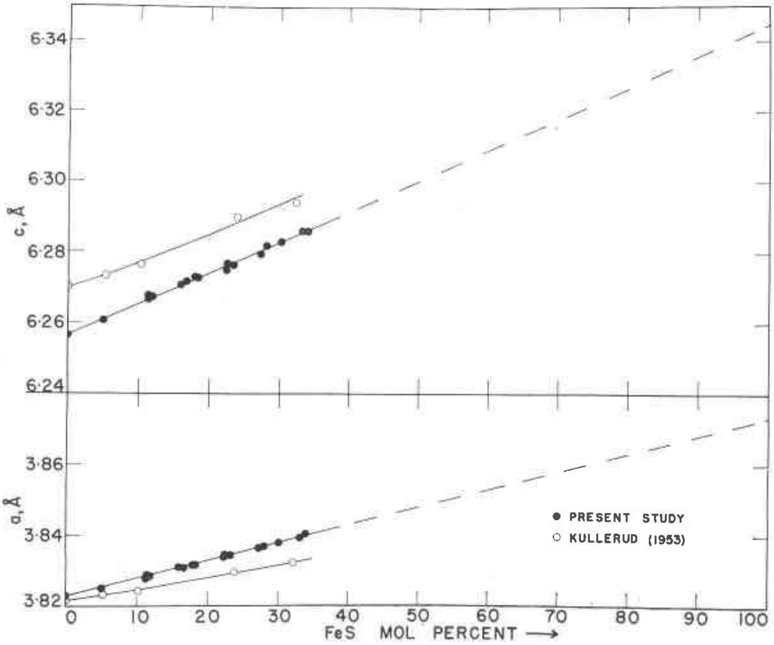

FIG. 1. Unit-cell edges, in Å, of Fe-bearing wurtzites.

TABLE 4. UNIT-CELL EDGES OF Fe-BEARING WURTZITES

FeS content		Temp. ° C.	Time (hours)	Unit-cell edges	
Weight per cent	Mol per cent			a, Å ±0.0006	c, Å ±0.001
4.57	5.04	1150	88	3.8250	6.2607
10.30	11.29	1150	48	3.8276	6.2678
10.31	11.30	1110	127	3.8286	6.2667
10.88	11.92	1150	88	3.8285	6.2674
14.56	15.89	1110	127	3.8310	6.2707
15.35	16.73	1150	88	3.8307	6.2719
16.46	17.92	1150	48	3.8316	6.2730
16.85	18.34	1110	127	3.8317	6.2727
20.64	22.38	1150	88	3.8340	6.2750
20.70	22.44	1150	48	3.8346	6.2769
21.57	23.36	1110	27	3.8345	6.2764
25.23	27.22	1150	88	3.8365	6.2795
26.05	28.08	1150	48	3.8369	6.2820
28.00	30.12	1110	27	3.8380	6.2829
30.89	33.13	1150	48	3.8394	6.2861
31.66	33.93	1150	88	3.8405	6.2860

slightly oxidized FeS as a starting material by Kullerud. The *c* versus composition curves, however, have a further serious and unexplained discrepancy, since Kullerud's curve lies significantly above that of the present study. The reason for the lack of agreement is unknown, but may, as suggested for the pure wurtzite measurements, be due to differences in measurement procedures.

Both the *a* and *c* values of Fe-bearing wurtzites change linearly with composition. Functions suitably describing these relations are:

$$a = 3.8230 + 0.000490X$$
$$c = 6.2565 + 0.000886X$$

where *a* and *c* are in Ångstrom units and X is the FeS content in mol per cent. These equations are derived from least squares analysis for the best fitting straight line that passes through the values for pure wurtzite. The standard deviation of measured values of *a* from the best fitting line is ±0.0004 Å; and of *c*, ±0.0007 Å. The cell edges of the hypothetical FeS compound with a wurtzite structure are, by extrapolation: $a=3.8720$ Å and $c=6.3451$ Å.

Mn-bearing wurtzites

An extensive, but discontinuous solid-solution series extends from wurtzite towards MnS. Kroger (1938) observed that the series was stable to at least 55 mol per cent MnS.

TABLE 5. UNIT-CELL EDGES OF Mn-BEARING WURTZITES

MnS content		Temp. ° C.	Time (hours)	Unit-cell edges		Sample prepared by[1]
Weight per cent	Mol per cent			a, Å ±0.0005	c, Å ±0.0008	
1.67	1.86	1200	120	3.8270	6.2603	B
2.33	2.60	1120	160	3.8274	6.2611	S
3.63	4.05	1200	120	3.8292	6.2671	B
4.30	4.79	1120	160	3.8310	6.2687	S
5.46	6.08	1200	120	3.8322	6.2709	B
6.46	7.18	1120	160	3.8350	6.2713	S
7.32	8.13	1120	160	3.8360	6.2737	S
7.35	8.16	1200	120	3.8357	6.2740	B
9.00	9.97	1200	120	3.8380	6.2777	B
9.48	10.50	1120	160	3.8400	6.2770	S
12.65	13.96	1120	160	3.8457	6.2858	S
13.70	15.10	1200	120	3.8475	6.2880	B
17.76	19.48	1120	160	3.8550	6.2966	S
18.37	20.13	1200	120	3.8561	6.3000	B
19.91	21.78	1120	160	3.8584	6.3000	S
27.63	29.95	1200	120	3.8718	6.3212	B
29.20	31.60	1120	160	3.8742	6.3205	S
37.27	39.96	1200	120	3.8888	6.3371	B
37.46	40.15	1120	160	3.8882	6.3411	S
43.91	46.72	1120	160	3.8990	6.3515	S
47.01	49.84	1200	120	3.9050	6.3618	B

[1] S refers to samples prepared by Skinner, B to those by Bethke.

The cell edges of Mn-bearing wurtzites determined in the present study are presented in Table 5 and graphically in Fig. 2. Similar measurements by Juza *et al.* (1956) and Smith *et al.* (1957) are also plotted. It is apparent that there is good agreement between the values obtained in the present study and those of Juza *et al.* (1956), but that serious disagreements arise with the data of Smith *et al.* (1957). Kroger (1938) stated that he observed a linear change of cell edges versus composition for Mn-bearing wurtzites, and that the projected linear plot passed through the measured cell edges of metastable hexagonal MnS.*

Our data also confirm the linearity of the relationships between both

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* Three modifications of MnS are known. A cubic form, metastable at room temperature, having a sphalerite-type structure; a hexagonal form, with a wurtzite-type structure, also believed metastable at room temperature, but recently reported in nature from thin manganiferous layers in marine, organic muds by Baron and Debyser (1957); and a second cubic form with a sodium chloride-type structure, occurring in nature as the mineral alabandite.

a and *c* and composition, but our projected *c* value for pure MnS is 0.02 Å higher than that measured by Schnaase (1933). Smith *et al.* (1957) on the other hand reported a discrepancy of 0.065 Å between their projected plot of *a* versus composition, assuming linearity, and the measured value of *a* for hexagonal MnS.

Kroger (1938), Juza *et al.* (1956) and the present study are in excellent agreement on the cell edges of Mn-bearing wurtzites, in spite of a diversity of preparation and measurement methods. It is suggested, therefore, that Smith *et al.* (1957) must be mistaken in the compositions they assign their synthetic wurtzites.

Least squares analysis of our data yield best fitting straight lines passing though the values for pure wurtzite that are described by the following equations:

$$a = 3.8230 + 0.001628Z$$

$$c = 6.2565 + 0.002089Z$$

where *a* and *c* are in Ångstrom units and Z is the MnS content in mol per cent. The standard deviation of measured values of *a* from the best fitting straight line is ±0.0005 Å, and of *c*, ±0.0011 Å. The extrapolated cell edges of pure MnS with a wurtzite structure are $a=3.9858$ Å and

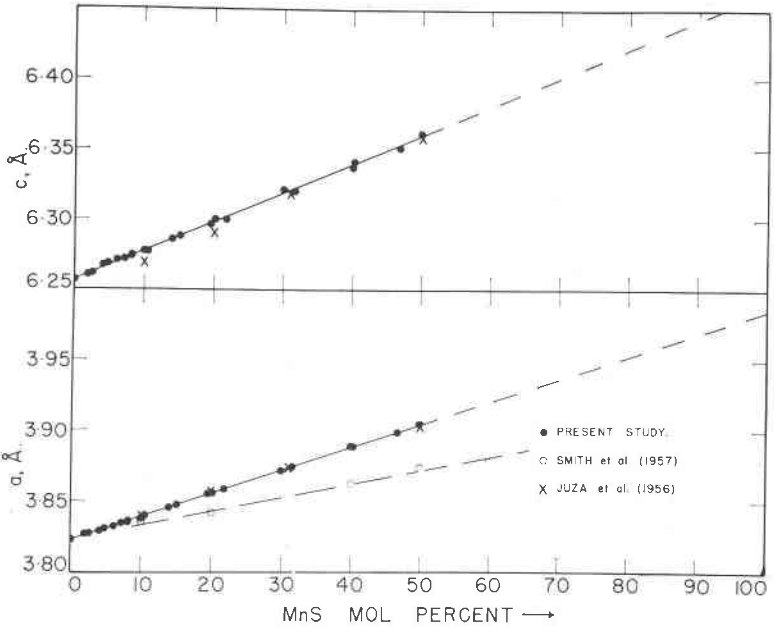

FIG. 2. Unit-cell edges, in Å, of Mn-bearing wurtzites.

TABLE 6. UNIT-CELL EDGES OF COMPOUNDS IN THE WURTZITE-GREENOCKITE SOLID-SOLUTION SERIES

CdS content		Temp. ° C.	Time (hours)	Unit-cell edges	
Weight per cent	Mol per cent			a, Å ±0.0006	c, Å ±0.001
5.12	3.51	965	162	3.8328	6.2736
9.59	6.68	965	162	3.8440	6.2888
10.03	6.99	1145	40	3.8430	6.2938
19.81	14.28	858	531	3.8674	6.3226
20.41	14.75	1145	40	3.8682	6.3238
34.46	26.18	1145	40	3.9020	6.3728
40.21	31.21	858	531	3.9194	6.4006
42.70	33.45	1145	40	3.9260	6.4068
50.23	40.50	1145	40	3.9507	6.4430
61.08	51.42	1145	40	3.9832	6.4938
69.32	60.38	1000	95	4.0112	6.5318
69.99	61.14	858	531	4.0136	6.5388
78.42	71.02	1145	40	4.0434	6.5804
79.60	72.47	1000	95	4.0482	6.5934
89.05	84.58	1000	95	4.0900	6.6398

$c = 6.4654$ Å. Schnaase (1933) measured the cell edges of pure MnS with a wurtzite-type structure and reported $a = 3.984$ Å,* in excellent agreement with our results; and $c = 6.445$ Å,* in poor agreement. The material measured by Schnaase was precipitated from an aqueous solution at low temperatures and was therefore subject to possible serious complications from polytypism. Since polytyping affects the measured c values much more strongly than it does the a values, little weight can be placed on Schnaase's determination of c.

Cd-bearing wurtzites

Kroger (1939), Hurlbut (1957) and others have demonstrated that a complete solid solution exists between wurtzite and greenockite (CdS). A number of compounds in the series were prepared in the present study and their cells edges measured. These data are presented in Table 6 and Fig. 3. Hurlbut (1957) presented a series of cell-edge measurements for the same solid-solution series. His data are in error, however (Hurlbut, written communication, 1959), as he incorrectly labeled the compositions of his synthetic compounds as mol per cent when actually they are in weight per cent. His measurements, converted to mol per cent, are plotted on Fig. 3. The plot of a versus composition is in excellent agree-

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* Converted from kX to Å.

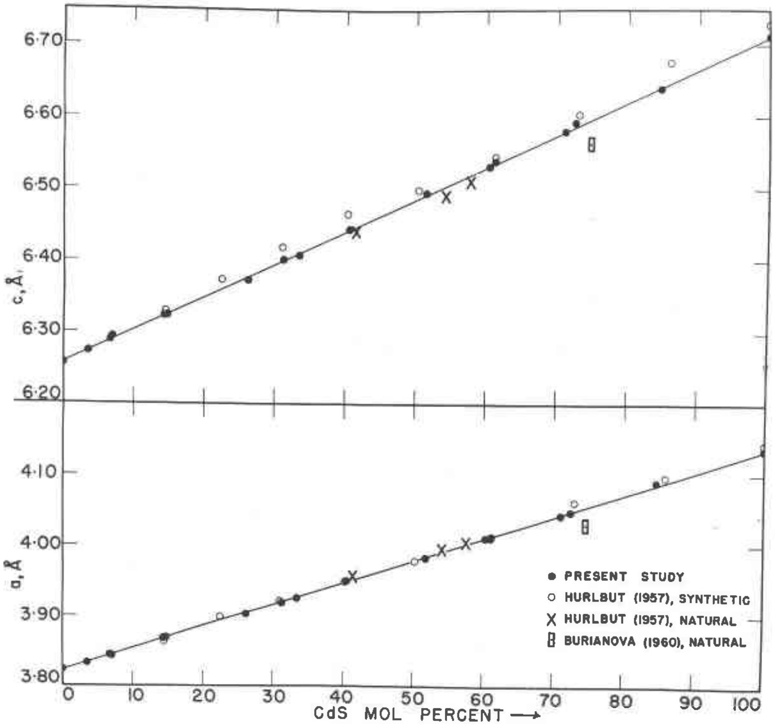

FIG. 3. Unit-cell edges, in Å, of compounds in the wurtzite-greenockite solid-solution series.

ment with that of the present study and also with the natural compounds described by Hurlbut (1957). The plot of *c* versus composition, however, is not in good agreement. A linear relation was found in the present study but all of Hurlbut's measurements fall above the observed line. The natural compounds reported by Hurlbut, however, are in good agreement with the synthetic compounds prepared in the present study. The curves are sensibly linear, the curvature observed by Hurlbut (1957) appearing only when compositions are expressed as weight per cent.

Burianova (1960) reports a zincian greenockite with the composition $(Cd_{0.746}Zn_{0.254})S$ from a sedimentary deposit at Tuva. The reported unit-cell edges are $a=4.030\pm0.004$ Å and $c=6.563\pm0.004$ Å.* Burianova's data fall somewhat below the unit-cell edge versus composition curves (Fig. 3) but, within the limits of measurement and analysis, must be considered in reasonable agreement with the synthetic compounds.

On plots of *a* and *c* versus CdS content, lines drawn through the values

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* Converted from kX to Å.

TABLE 7. UNIT-CELL EDGES OF Fe-BEARING GREENOCKITES

FeS content		Temp. ° C.	Time (hours)	Unit-cell edges	
Weight per cent	Mol per cent			a, Å ±0.0008	c, Å ±0.001
5.55	8.81	900	238	4.1158	6.6826
10.58	16.28	800	431	4.0954	6.6543
15.38	22.59	900	238	4.0752	6.6243
19.79	28.85	800	431	4.0644	6.6037
25.50	36.00	900	238	4.0400	6.5780
30.59	42.00	950	238	4.0280	6.5490
35.18	47.14	950	238	4.0078	6.5400

for pure wurtzite and pure greenockite also fit the observed values of the various intermediate compositions rather well. Because of the good fit and the minimum compositional uncertainty of the pure end members, these relationships have been chosen to describe our data. The corresponding functions defining the variation in cell dimensions with composition are:

$$a = 3.8230 + 0.003124Y$$
$$c = 6.2565 + 0.004555Y$$

where a and c are in Ångstrom units, and Y is the CdS content in mol per cent. The equations fit our data to ±0.001 Å for a and ±0.003 Å for c.

Fe-bearing greenockites

An extensive but incomplete solid-solution series, having a wurtzite structure, extends from greenockite towards FeS. Fe-rich greenockites containing up to 47 mol per cent FeS were prepared at high temperatures and quenched to room temperature. The iron replaces cadmium in the greenockite structure, with a resultant marked decrease in the cell edges of the greenockite. Measurements demonstrating this effect are presented in Table 7, and graphically in Fig. 4. It is apparent that within the limits of measurement error the decrease in cell edges with increasing FeS content must be considered linear.

On plots of a and c versus FeS content, lines drawn through the values for pure CdS and for FeS with a wurtzite structure (obtained by extrapolation of the Fe-bearing wurtzite data presented above) fit our data well. The functions are:

$$a = 4.1354 - 0.002634W$$
$$c = 6.7120 - 0.003669W$$

where *a* and *c* are in Ångstrom units and W is the FeS content in mol per cent. The functions define both *a* and *c* to ±0.003 Å.

Kroger (1939) demonstrated that greenockite can accommodate extensive replacement of Cd by Mn in the structure. He further states that the observed reductions in cell edges consequent on this replacement are identical with those computed on the assumption of additivity of the unit-cell edges of hexagonal CdS and hexagonal MnS. Apparently then, both FeS and MnS cause linear decreases in the cell edges of greenockite.

TERNARY WURTZITES

Fe- plus Mn-bearing wurtzites

During the course of systematic phase-equilibria studies a number of wurtzites whose compositions fall in the ternary composition plane ZnS-FeS-MnS were prepared. The cell edges of these compounds have been measured and are presented in Table 8. Also given in Table 8 are the cell edges calculated on the assumption of additivity using the functions developed for the binary solid solutions above. It can be seen that the agreement between the calculated and experimental values of *a* is

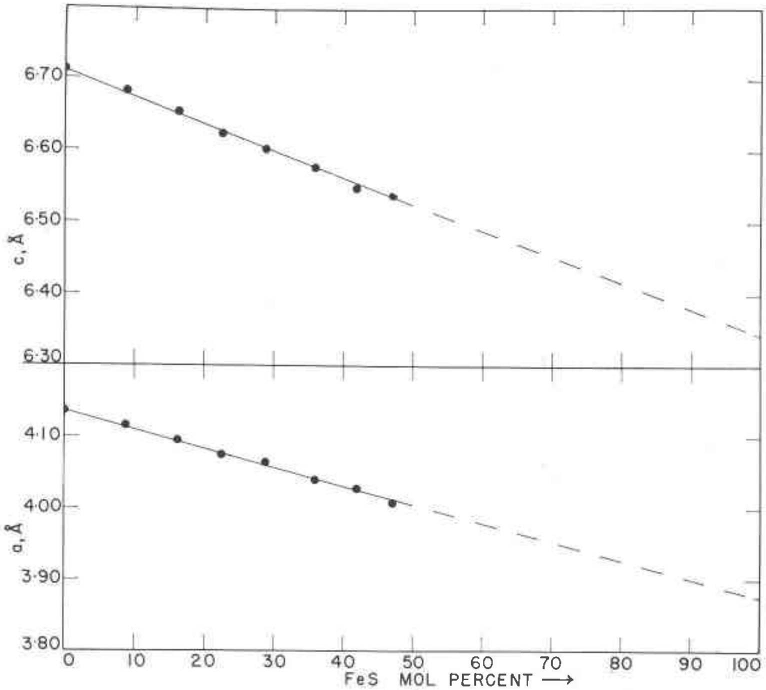

FIG. 4. Unit-cell edges of Fe-bearing greenockites.

TABLE 8.—UNIT-CELL EDGES OF Fe- PLUS Mn-BEARING WURTZITES

Composition						Temp. ° C.	Time (hours)	Unit-cell edges					
Weight per cent			Mol per cent					a, Å			c, Å		
ZnS	FeS	MnS	ZnS	FeS	MnS			Measured ±0.001	Calculated	Difference $\times 10^4$	Measured ±0.002	Calculated	Difference $\times 10^4$
88.18	6.16	5.66	87.01	6.74	6.25	1150	48	3.8368	3.8365	+ 3	6.2759	6.2755	+ 4
87.47	6.87	5.66	86.24	7.51	6.25	1100	127	3.8370	3.8369	+ 1	6.2766	6.2761	+ 5
84.56	7.18	8.24	83.11	7.82	9.07	800	450	3.8410	3.8416	− 6	6.2785	6.2823	−38
84.26	4.97	10.77	82.75	5.40	11.85	800	450	3.8453	3.8449	+ 4	6.2806	6.2861	−55
82.13	13.01	4.86	80.52	14.14	5.34	1100	127	3.8390	3.8386	+ 4	6.2788	6.2802	−14
82.09	12.87	5.04	80.48	13.99	5.53	1150	48	3.8391	3.8388	+ 3	6.2786	6.2805	−19
80.86	7.97	11.17	79.12	8.64	12.24	1100	127	3.8466	3.8471	− 5	6.2846	6.2897	−51
80.59	7.33	12.08	78.82	7.95	13.23	1100	127	3.8488	3.8484	+ 4	6.2866	6.2911	−45
79.87	12.95	7.18	78.10	14.04	7.86	800	240	3.8440	3.8427	+13	6.2815	6.2853	−38
79.40	10.40	10.20	77.58	11.26	11.16	1150	48	3.8480	3.8467	+13	6.2849	6.2898	−49
78.79	10.00	11.21	76.93	10.82	12.25	800	240	3.8487	3.8482	+ 5	6.2923	6.2917	+ 6
77.74	8.12	14.14	75.78	8.78	15.44	800	240	3.8525	3.8524	+ 1	6.2941	6.2965	−24
77.68	13.16	9.16	75.76	14.23	10.01	800	456	3.8470	3.8463	+ 7	6.2887	6.2900	−13
77.54	15.31	7.15	75.64	16.55	7.81	800	765	3.8450	3.8438	+12	6.2856	6.2875	−19
77.52	14.06	8.41	75.61	15.20	9.19	800	456	3.8455	3.8454	+ 1	6.2896	6.2892	+ 4
75.63	11.97	12.40	73.58	12.91	13.51	1100	127	3.8512	3.8513	− 1	6.2932	6.2961	−29
74.48	9.93	15.59	72.35	10.69	16.96	1150	48	3.8555	3.8558	− 3	6.2959	6.3014	−55
74.32	20.74	4.94	72.27	22.35	5.38	1100	48	3.8423	3.8428	− 5	6.2857	6.2875	−18
73.51	20.39	6.10	71.41	21.95	6.64	1100	127	3.8450	3.8446	+ 4	6.2872	6.2898	−26
72.65	2.75	24.60	70.36	2.96	26.68	1100	127	3.8668	3.8678	−10	6.3100	6.3148	−48
72.18	21.59	6.23	70.02	23.21	6.77	800	765	3.8460	3.8454	+ 6	6.2890	6.2912	−22
70.12	21.96	7.92	67.86	23.56	8.58	800	765	3.8482	3.8485	− 3	6.2955	6.2953	+ 2
69.66	9.97	20.37	67.29	10.67	22.04	1150	48	3.8588	3.8641	+53	6.3098	6.3119	−21
69.66	7.97	22.37	67.27	8.53	24.20	1100	127	3.8652	3.8666	−14	6.3110	6.3147	−37
68.92	21.48	9.60	66.60	23.01	10.39	1150	48	3.8503	3.8512	− 9	6.2974	6.2986	−12
65.33	19.36	15.31	62.86	20.64	16.50	1150	48	3.8606	3.8600	+ 6	6.3085	6.3093	− 8
64.62	20.24	15.14	62.13	21.57	16.30	1150	48	3.8610	3.8601	+ 9	6.3052	6.3096	−44
63.77	11.26	24.97	61.19	11.98	26.83	1150	48	3.8714	3.8726	−12	6.3197	6.3231	−34
60.14	22.82	17.04	57.54	24.21	18.25	800	456	3.8655	3.8646	+ 9	6.3176	6.3160	+16
60.09	19.73	20.18	57.47	20.91	21.62	1150	48	3.8667	3.8684	−17	6.3194	6.3202	− 8
59.78	21.04	19.18	57.17	22.29	20.54	800	456	3.8685	3.8673	+12	6.3186	6.3191	− 5
59.63	9.61	30.76	56.94	10.17	32.89	1150	48	3.8797	3.8815	+18	6.3318	6.3342	−24
58.73	27.99	13.28	56.13	29.65	14.22	1100	127	3.8584	3.8607	+23	6.3090	6.3125	−35
55.08	9.88	35.04	52.32	10.40	37.28	1150	48	3.8876	3.8888	−12	6.3411	6.3436	−25

close, the standard deviation being less than ±0.001 Å. The experimental c values, although in relatively good agreement, in general fall below the calculated values. However, there is no obvious systematic relationship between composition and deviation of the experimental values of c from those calculated from the binary relationships. Certainly, to a reasonable approximation, the additivity assumption adequately describes the relationship between composition and unit-cell edges.

The functions used to calculate the cell dimensions of the ternary wurtzites are:

$$a = 3.8230 + 0.000490X + 0.001628Z$$
$$c = 6.2565 + 0.000886X + 0.002089Z$$

where X and Z are the FeS and MnS contents in mol per cent respectively.

Kroger (1939) observed additivity for a versus composition in the system ZnS-CdS-MnS. He states, however, "the c-axis experimental values were slightly greater than the calculated ones; in the center of the system the difference was about 0.03 Å, decreasing continuously in the direction of the pure substances."

It is apparent, then, that in both ternary systems, ZnS-FeS-MnS and ZnS-CdS-MnS, Vegard's Law (the assumption of additivity) does hold for a but at best can only be considered an approximation in the case of c.

Fe- plus Cd-bearing wurtzites

Compounds having the wurtzite structure can be prepared across much of the composition plane ZnS-FeS-CdS. Four ternary compounds were prepared during the present study, sufficient only to check the assumption of additivity. The results are presented in Table 9. It is immediately apparent that compounds in the system do obey Vegard's Law and hence that functions defining a and c in the ternary compounds can be derived by simple addition from the binary functions, so that

$$a = 3.8230 + 0.000490X + 0.003124Y$$
$$c = 6.2565 + 0.000886X + 0.004555Y$$

where a and c are in Ångstrom units and X and Y are the FeS and CdS contents respectively in mol per cent. Calculated values of a and c using these functions are presented in Table 9 for comparison with the measured values.

CONCLUSIONS

The unit-cell edges of all compounds having the wurtzite (2H) structure, with compositions lying in the ternary planes ZnS-FeS-MnS and

TABLE 9. UNIT-CELL EDGES OF Fe- PLUS Cd-BEARING WURTZITES

Composition						Temp. ° C.	Time (hours)	Unit-cell edges					
Weight per cent			Mol per cent					a, Å			c, Å		
ZnS	FeS	CdS	ZnS	FeS	CdS			Measured ±0.001	Calculated	Difference ×10^4	Measured ±0.002	Calculated	Difference ×10^4
74.21	8.30	17.49	77.95	9.66	12.39	1100	70	3.8674	3.8664	+10	6.3227	6.3215	+12
50.19	30.21	19.60	51.80	34.56	13.64	1100	70	3.8830	3.8825	+ 5	6.3484	6.3492	− 8
29.99	19.78	50.23	34.96	25.55	39.49	1100	70	3.9586	3.9589	− 3	6.4592	6.4590	+ 2
10.11	20.39	69.50	12.70	28.40	58.90	1100	70	4.0220	4.0219	+ 1	6.5490	6.5500	−10

ZnS-FeS-CdS, are linear functions of their compositions expressed in mol per cent. Wurtzite structure-type compounds in the plane ZnS-CdS-MnS were found by Kroger (1939) to have a linear relation between *a* and composition, but to have small departures from linearity at high CdS plus MnS content in the case of *c*.

It is a reasonable conclusion therefore that a linear relation exists between *a* and compositions expressed in mol per cent for the wurtzite structure-type compounds whose compositions can be expressed in terms of the components ZnS, FeS, MnS, and CdS. The function defining this relation is:

$$a = 3.8230 + 0.000490X + 0.003124Y + 0.001628Z$$

where *a* is in Å and X, Y, and Z are the FeS, CdS, and MnS contents in mol per cent respectively. The function should define *a* to ±0.001 Å.

Because of Kroger's observations on the small departures from linearity of *c* versus composition in the plane ZnS-CdS-MnS, the assumption of additivity for *c*, of wurtzite structure-type compounds in the quaternary system ZnS-FeS-MnS-CdS, can only be considered approximate. The maximum systematic deviation observed by Kroger was 0.03 Å, and if we make the assumption that this is the maximum deviation in the system, the function:

$$c = 6.2565 + 0.000886X + 0.004555Y + 0.002089Z$$

where *c* is in Å and X, Y, and Z are the FeS, CdS, and MnS contents in mol per cent respectively, should be true to ±0.03 Å.

The uncertainty raised by Kroger's observations clearly suggests that the *a* versus composition function is a more suitable one to use in determining the compositions of wurtzites from their unit-cell edges.

References

Allen, E. T., and Crenshaw, J. L., 1912, The sulphides of Zn, Cd and Hg; their crystalline forms and genetic significance: *Am. Jour. Sci., Ser. 4,* **34,** 341–396.

Baron, G., and Debyser, J., 1957, Sur la présence dans des vases organiques de la mer Baltique, du sulfure manganese β hexagonal: *Acad. sci. Paris Comptes rendus,* **245,** 1148–1160.

Bragg, W. L., 1920, The crystalline structure of zinc oxide: *Phil. Mag.,* **39,** 647.

———, 1947, The conversion factor for kX units to Ångstrom units: *Am. Mineral,* **32,** 592.

Burianova, E. Z., 1960, On the mineralogy and geochemistry of cadmium in sedimentary rocks of Tuva: *Geokhimiya, no. 2,* 177–182.

Frondel, Clifford, 1955, A precision *x*-ray powder camera: *Am. Mineral.,* **40,** 876–884.

——— and Palache, Charles, 1950, Three new polymorphs of zinc sulfide: *Am. Mineral.,* **35,** 29–42.

Fuller, M. L., 1929, The crystal structure of wurtzite: *Phil. Mag.,* **8,** 658–663.

Hurlbut, C. S., Jr., 1957, The wurtzite-greenockite series: *Am. Mineral.,* **42,** 184–190.

International Tables for *X*-Ray Crystallography, 1952, Kynoch Press, Birmingham, England.

JUZA, R., RABENAU, A., AND PASCHER, G., 1956, Über feste Lösungen in den Systemen ZnS/MnS, ZnSe/MnSe, ZnTe/MnTe: *Zeit. Anorg. und allgem. Chemie*, **285**, 61–69.

KROGER, F. A., 1938, Formation of Solid Solutions in the System Zincsulfide-Manganesesulfide: *Zeit. Krist.*, **A100**, 543–545.

———, 1939, Solid solutions in the ternary system ZnS-CdS-MnS: *Zeit. Krist.*, **A102**, 132–135.

KULLERUD, GUNNAR, 1953, The FeS-ZnS system. A geologic thermometer: *Norsk geol. tidsskr.*, **32**, 61–147.

SCHNAASE, H., 1933, Kristallstruktur der Manganosulfid und ihrer Mischkristalle mit Zinksulfid und Cadmiumsulfid: *Zeit. phys. chemie*, **B20**, 89–117.

SKINNER, B. J., 1961, Unit-cell edges of natural and synthetic sphalerites: *Am. Mineral.* This issue.

SKINNER, B. J., AND BARTON, P. B., JR., 1960, The substitution of oxygen for sulfur in wurtzite and sphalerite: *Am. Mineral.*, **45**, 612–625.

SKINNER, B. J., BARTON, P. B., JR., AND KULLERUD, G., 1959, Effect of FeS on the unit cell edge of sphalerite. A revision: *Econ. Geology*, **54**, 1040–1046.

SMITH, F. G., 1955, Lattice constants of cadmium sulfide: *Am. Mineral.*, **40**, 696–697.

———, DASGUPTA, S. K., AND HILL, V. G., 1957, Manganoan ferroan wurtzite from Llallagua, Bolivia (1): *Canadian Mineral.*, **6**, 128–135.

STROCK, L. W., AND BROPHY, V. A., 1955, Synthetic zinc sulfide polytype crystals: *Am. Mineral.*, **40**, 94–106.

SWANSON, H. E., AND FUYAT, R. K., 1953, Standard *x*-ray diffraction powder patterns. Volume II: *Nat. Bur. Stds. Circ.* **539**, 65 pp.

———, ——— AND UGRINIC, G. M., 1955, Standard *x*-ray diffraction powder patterns. Volume IV: *Nat. Bur. Stds. Circ.* **539**, 75 pp.

ULRICH, F., AND ZACHARIASEN, W., 1925, Über die Kristallstruktur des α- und β-Cds, sowie des Wurtzits: *Zeit. Krist.*, **62**, 260–273.

WYCKOFF, R. W. G., 1948, Crystal structures: Interscience.

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