

## UNIT-CELL EDGES OF NATURAL AND SYNTHETIC SPHALERITES\*

BRIAN J. SKINNER, *U. S. Geological Survey, Washington, D. C.*

### ABSTRACT

The unit-cell edges of a number of synthetic Fe-, Mn-, and Cd-bearing sphalerites have been measured. The effects of the components in solid solution on the unit-cell edge of sphalerite are linear and additive. The unit-cell edge of a sphalerite can be expressed in terms of its composition by the function  $a = 5.4093 + 0.000456X + 0.00424Y + 0.00202Z$ , where X, Y, and Z are the contents of FeS, CdS, and MnS in mol per cent and  $a$  is in Ångströms.

Measurements of nineteen analyzed natural sphalerites show good agreement with the synthetic materials.

### INTRODUCTION

Sphalerite (ZnS) is cubic, space group  $F\bar{4}3m$ ,  $Z=4$ , with a unit-cell edge ( $a$ ) at 25° C. of  $5.4093 \pm 0.0002$  Å (Skinner and Barton, 1958 and 1960).

Sphalerite does not deviate measurably from the stoichiometric formula, although it can tolerate extensive solid solutions in which the zinc is replaced by other cations such as iron, manganese, cadmium, and copper (Kullerud, 1953). Anionic substitutions may also occur, whereby elements such as selenium and oxygen (Skinner and Barton, 1960) may replace the sulfur. In the present study care has been exercised to prevent any anionic substitutions.

The individual substitutions of iron, manganese, and cadmium for zinc in the sphalerite structure have been studied in the past, the most detailed and recent study being that of Kullerud (1953), and for the effect of iron alone, Skinner *et al.* (1959). In these studies it has been amply demonstrated that a precise determination of the cell edge of sphalerite provides a sensitive measure of composition.

As a portion of a larger study on phase relations in the system ZnS-FeS-MnS and ZnS-FeS-CdS, the cell edges of a number of synthetic and natural sphalerites have been determined.

### SAMPLE PREPARATION

Charges of appropriate composition were prepared by weighing together the requisite amounts of ZnS, FeS, MnS, and CdS. The ZnS and FeS were prepared from the same zinc, iron, and sulfur, and in the same manner, as described by Skinner and Barton (1960). MnS was prepared from metallic manganese (Johnson, Matthey and Co. Ltd., Laboratory No. 3770, Catalogue No. J. M. 810, Table 1) and sulfur. Stoichiometric

\* Publication authorized by the Director, U. S. Geological Survey.

TABLE 1. SEMIQUANTITATIVE SPECTROGRAPHIC ANALYSES OF MANGANESE  
(BY JOHNSON, MATTHEY AND CO. LTD.), AND CdS (ANALYSIS  
BY K. V. HAZEL, U. S. GEOLOGICAL SURVEY)

Element	Mn	CdS	Element	Mn	CdS
Si	0.0002%	0.015%	Cd	—	Major
Al	—	0.0015	Cr	—	0.0003
Fe	0.0003	0.07	Cu	0.0001	0.015
Mg	0.001	0.03	Ni	—	0.003
Ca	<0.0001	0.03	Pb	—	0.0015
Mn	Major	—	Sr	—	0.0003
Ag	—	0.000015	V	—	0.0015
Ba	—	0.0015	Zn	—	0.15
Bi	—	0.0015			

Specifically sought, but not detected: As, Au, B, Be, Co, Cs, Ga, Ge, Hf, Hg, In, Ir, K, Li, Mo, Na, Nb, Os, P, Pt, Rb, Re, Rh, Ru, Sb, Se, Sn, Ta, Te, Ti, Tl, W, Zr.

mixtures of manganese and sulfur were weighed into silica-glass tubes; then the evacuated and sealed tubes were heated at 800° C. for 48 hours. To ensure complete reaction the tubes were opened after 48 hours, the contents ground, a slight excess of sulfur added and the charge reheated at 800° C. for a further 48 hours. There is no indication that MnS<sub>2</sub> is formed by the excess sulfur. Excess sulfur in the final product was removed by washing with carbon disulfide.

CdS was obtained as a fine yellow powder from British Drug Houses Ltd. Analysis of this material (Table 1) showed it to be pure, but as a handling precaution it was always recrystallized in sealed silica-glass tubes at 900° C. for 24 hours. This produced a larger grain size and consequently led to easier handling during weighing procedures.

The preparation of Fe-bearing sphalerite has been discussed in detail by Kullerud (1953) and by Skinner *et al.* (1959). Exactly the same methods as those described by Skinner were used to produce the sphalerites for the present study.

#### UNIT-CELL EDGE MEASUREMENT

All *x*-ray measurements of the cell edges reported in this study were made in exactly the same manner, using the same equipment and internal standards, as reported by Skinner and Barton (1960) and Skinner *et al.* (1959). The precision stated for measurements is the maximum observed deviation from a numerical average of repetitive measurements and is therefore a non-statistical statement of the range. 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).

All measurements were made at a room temperature of  $25^{\circ} \pm 3^{\circ}$  C. Thermal expansion data for sphalerite (Birch *et al.*, 1942) and calculations based on these data indicate the variation in cell edge of sphalerite per degree centigrade to be 0.00004 Å. The uncertainty introduced by making cell edge measurements at room temperature and not introducing a correction factor for thermal expansion is thus only  $\pm 0.0001$  Å, a figure significantly less than the reproducibility of measurement.

#### UNIT-CELL EDGES OF SYNTHETIC BINARY SPHALERITES

The effect of FeS on the unit-cell edge of sphalerite was discussed, and previous studies summarized, by Skinner *et al.* (1959). They derived the linear function  $a = 5.4093 + 0.000456X$ , where  $a$  is the cell edge, in Ångstrom units, of a sphalerite containing  $X$  mole per cent FeS.

The cell edges of a number of Mn- and Cd-bearing sphalerites have been measured in the present investigation and data for these are presented in Tables 2 and 3. The cell edges of both Mn- and Cd-bearing sphalerites change linearly with composition (Fig. 1).

CdS is known in two polymorphic modifications; a hexagonal type with a wurtzite structure (greenockite), and a cubic modification with a sphalerite structure, found in nature as the mineral hawleyite (Traill and Boyle, 1955). The cell edge of the cubic modification of CdS has been

TABLE 2. UNIT-CELL EDGES OF Cd-BEARING SPHALERITES

Composition, CdS		Temp. ° C.	Time (hours)	Unit-cell edge $a$ , Å
Weight per cent	Mol per cent			
0.83	0.56	880	400	5.4116 $\pm$ 0.0003
1.19	0.81	880	400	5.4124 $\pm$ 0.0003
1.64 <sup>1</sup>	1.11	650	7800	5.4143 $\pm$ 0.0003
2.33	1.58	880	400	5.4160 $\pm$ 0.0003
2.94	2.00	880	400	5.4172 $\pm$ 0.0003
3.17 <sup>1</sup>	2.16	650	7800	5.4186 $\pm$ 0.0003
4.03	2.75	850	350	5.4205 $\pm$ 0.0003
5.01 <sup>1</sup>	3.47	650	7800	5.4229 $\pm$ 0.0004
5.30	3.64	750	450	5.4244 $\pm$ 0.0004
7.13	4.92	750	450	5.4300 $\pm$ 0.0003
8.89 <sup>1</sup>	6.18	650	7800	5.4354 $\pm$ 0.0004

<sup>1</sup> Samples prepared by Paul B. Barton Jr., and cell edges measured by P. M. Bethke.

TABLE 3. UNIT-CELL EDGES OF Mn-BEARING SPHALERITES

Composition, MnS		Temp. ° C.	Time (hours)	Unit-cell edge <i>a</i> , Å
Weight per cent	Mol per cent			
1.06	1.19	850	350	5.4116 ± 0.0003
1.24	1.39	880	400	5.4117 ± 0.0003
1.98	2.21	850	350	5.4140 ± 0.0005
2.06	2.30	880	400	5.4140 ± 0.0006
2.93	3.27	880	400	5.4155 ± 0.0005
3.82	4.26	850	350	5.4172 ± 0.0003
5.06	5.63	880	400	5.4196 ± 0.0003
5.18	5.77	750	450	5.4200 ± 0.0003
6.01	6.68	750	450	5.4216 ± 0.0003
7.20	7.99	750	450	5.4236 ± 0.0003

measured by Goldschmidt (1927) who reported  $a = 5.823 \pm 0.005$  kX, and by Ulrich and Zachariasen (1925) who reported  $a = 5.820$  kX. Converted to Å by the kX/Å conversion factor, 1.00202, these values become  $5.835 \pm 0.005$  Å and  $5.832$  Å respectively. Selecting  $5.833 \pm 0.005$  Å as a reasonable average value for  $a$  of cubic CdS, the cell edges of the Cd-bearing sphalerites prepared in the present study fall on the straight line joining  $a$  for pure sphalerite (5.4093) and  $a$  for cubic CdS. The function relating the cell edge of Cd-bearing sphalerites with composition is  $a = 5.4093 + 0.00424Y$  where  $Y$  is the CdS content in mol per cent, and  $a$  is in Ångstrom units. The standard deviation of measured values of  $a$  from the straight line is  $\pm 0.0003$  Å.

The sphalerite-structure type modification of MnS is not known to occur in nature but may be prepared as an unstable compound at room temperature. Schnaase (1932) demonstrated that homogeneous sphalerite-type solid solutions could be prepared in the system ZnS-MnS, with an interruption between 89 and 20 mol per cent MnS, by precipitation from aqueous solutions. He also reported a cell edge of  $5.600 \pm 0.002$  kX for the sphalerite form of MnS (Schnaase, 1932). This converts to  $5.611 \pm 0.002$  Å.

The cell edges of the Mn-bearing sphalerites measured in the present study fall on, or close to, the straight line joining 5.4093 ( $a$  for pure sphalerite) and 5.611, indicating that Mn-bearing sphalerites obey Vegard's law within the limits of measurement. The equation for this line, which defines the cell edge of Mn-bearing sphalerite is  $a = 5.4093 + 0.00202Z$ , where  $Z$  is the MnS content in mol per cent,  $a$  is the cell edge

in Å. The standard deviation of measured values of  $a$  from the straight line is  $\pm 0.0003$  Å.

Kullerud (1953) also related the change of cell edge of sphalerite with its cadmium and manganese contents. Kullerud's data contain numerical errors in the conversion of weight per cent to mol per cent and his cell edge measurements which are reported in Å are actually in kX units. The conversion from kX to Å can be made by applying the kX/Å conversion factor 1.00202 (Bragg, 1947). The corrected values for Kullerud's measurements are presented in Table 4. Agreement between the present measurements and those of Kullerud (1953), considering the precision of measurement in each case, is poor (Fig. 1). Initial Mn- and Cd-bearing sphalerites prepared for this study had cell edges in excellent agreement with those of Kullerud. However, my colleague, Philip M. Bethke, could not satisfactorily reproduce these results. This apparent inconsistency led to the suspicion that the synthetic preparations used may have been inhomogeneous and hence that the measured cell edges were spurious. Further work by Bethke and by the writer confirmed this suspicion. The inhomogeneity develops because the MnS and CdS grains loaded into the capsules saturate the ZnS grains nearest them. Further diffusion of the Mn and Cd, leading to a homogeneous charge, is apparently slow. This

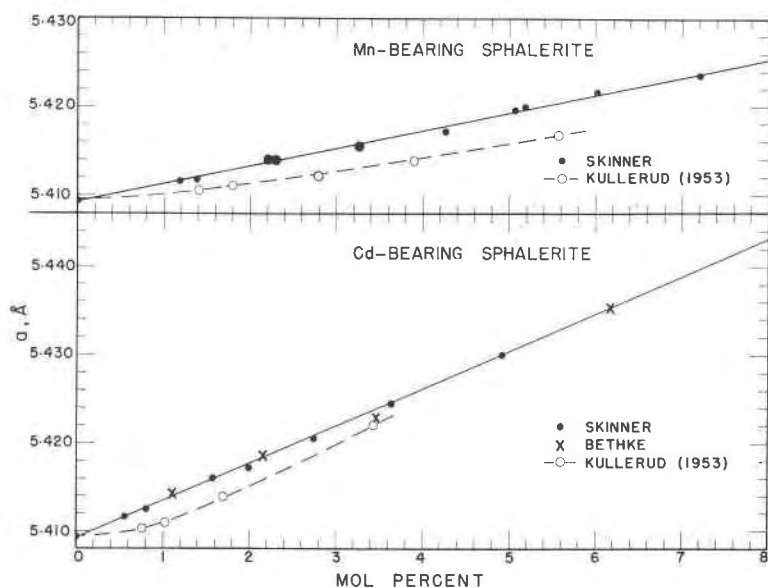


FIG. 1. Relation between unit-cell edge and composition of Mn- and Cd-bearing sphalerite.

TABLE 4. UNIT-CELL EDGES OF Mn- AND Cd-BEARING SPHALERITES DETERMINED BY KULLERUD (1953), CONVERTED FROM kX TO Å UNITS AND CORRECTED FOR ERRORS IN MOL PER CENT CALCULATIONS

Composition		Unit-cell edge $a$ , Å	
MnS Weight per cent	MnS Mol per cent	Original	Corrected
0	0	5.3985 ± 0.0001	5.4094 ± 0.0001
1.25	1.40	5.3996 ± 0.0003	5.4105 ± 0.0003
1.80	2.01	5.4002 ± 0.0003	5.4111 ± 0.0003
2.50	2.79	5.4013 ± 0.0003	5.4122 ± 0.0003
3.50	3.90	5.4030 ± 0.0003	5.4139 ± 0.0003
5.00	5.57	5.4059 ± 0.0003	5.4168 ± 0.0003
CdS Weight per cent	CdS Mol per cent		
1.10	0.76	5.3994 ± 0.0003	5.4103 ± 0.0003
1.50	1.02	5.4000 ± 0.0003	5.4109 ± 0.0003
2.50	1.70	5.4030 ± 0.0003	5.4139 ± 0.0003
5.00	3.43	5.4112 ± 0.0003	5.4221 ± 0.0003

effect can be minimized in several ways. First, by using well-mixed, finely ground starting materials. Second, by working at the highest possible temperatures at which sphalerite of the desired composition is stable (that is, just below the temperature at which a wurtzite phase first appears). Third, if the capsule is opened after several days heating, the contents very finely ground (preferably under acetone to prevent loss of any particles) and the ground charge replaced and reheated under the same conditions, equilibration occurs much more rapidly. The inhomogeneity is most marked when the starting ZnS, CdS and MnS are in coarse grains and at low CdS and MnS concentrations. It seems probable that this effect gives rise to the "hooks" previously observed in the cell edge versus composition curves for Mn- and Cd-bearing sphalerites.

The measurements reported in this paper represent the relations for homogeneous compounds. Because the initial compounds prepared in this study were inhomogeneous and gave non-linear cell edge versus composition curves, it seems probable that the compounds measured by Kullerud (1953), who also obtained non-linear curves, were inhomogeneous.

UNIT-CELL EDGES OF SYNTHETIC TERNARY SPHALERITES

Fe- plus Mn-bearing sphalerites were prepared over a wide range of compositions, and the cell edges measured. These data are gathered in Table 5 and presented diagrammatically in Fig. 2. Contours of equal *a* are, within the limits of error of the data, straight lines. The contours are essentially parallel throughout the composition range studied.

Fe- plus Cd-bearing sphalerites also have an essentially linear relation between the cell edge and composition (Table 6, Fig. 3). The contours of equal *a* are straight lines, and are essentially parallel. Thus the cell edges of both Fe- plus Mn- and Fe- plus Cd-bearing sphalerites are linear functions of their compositions and obey Vegard's law.

It is a reasonable assumption that the cell edges of Fe- plus Mn- plus Cd-bearing sphalerites should also be linear functions of their composi-

TABLE 5. UNIT-CELL EDGES OF Fe- PLUS Mn-BEARING SPHALERITES

Composition						Temp. ° C.	Time (hours)	Unit-cell edge, <i>a</i> , Å		
Weight per cent			Mol per cent					Meas- ured ± 0.0004	Calcu- lated	Differ- ence
ZnS	FeS	MnS	ZnS	FeS	MnS					
95.74	2.61	1.65	95.28	2.88	1.84	750	912	5.4143	5.4143	0.0000
94.28	5.22	0.50	93.69	5.75	0.56	922	305	5.4126	5.4130	+0.0004
93.84	2.23	3.93	93.17	2.46	4.37	750	912	5.4192	5.4192	0.0000
93.27	4.53	2.20	92.57	4.98	2.45	750	912	5.4164	5.4165	+0.0001
92.87	3.61	3.52	92.12	3.97	3.91	750	912	5.4190	5.4190	0.0000
92.63	2.78	4.59	91.84	3.06	5.10	750	912	5.4210	5.4210	0.0000
91.54	7.56	0.90	90.70	8.30	1.00	830	403	5.4148	5.4151	+0.0003
90.33	4.53	5.14	89.34	4.97	5.69	830	603	5.4238	5.4231	-0.0007
90.02	6.39	3.59	89.02	7.00	3.98	750	912	5.4201	5.4205	+0.0004
87.97	11.58	0.45	86.83	12.67	0.50	922	305	5.4155	5.4161	+0.0006
86.34	11.57	2.09	85.06	12.64	2.30	750	912	5.4210	5.4197	-0.0013
85.80	9.00	5.20	84.44	9.82	5.74	750	800	5.4245	5.4254	+0.0009
83.24	12.03	4.73	81.73	13.08	5.19	830	603	5.4255	5.4258	+0.0003
83.12	12.88	4.00	81.59	14.01	4.40	750	800	5.4243	5.4246	+0.0003
82.04	16.21	1.75	80.46	17.62	1.92	750	800	5.4213	5.4212	-0.0001
81.16	17.16	1.68	79.52	18.64	1.84	750	800	5.4213	5.4215	+0.0002
80.93	18.24	0.83	79.28	19.81	0.91	830	603	5.4202	5.4201	-0.0001
80.04	16.82	3.14	78.32	18.24	3.44	750	800	5.4245	5.4245	0.0000
79.63	17.24	3.13	77.88	18.69	3.43	800	240	5.4244	5.4247	+0.0003
78.93	16.69	4.38	77.13	18.08	4.79	830	603	5.4273	5.4272	-0.0001
78.46	21.13	0.41	76.67	22.88	0.45	830	603	5.4204	5.4206	+0.0002
78.00	19.00	3.00	76.16	20.56	3.28	800	480	5.4253	5.4253	0.0000
77.47	18.39	4.14	75.58	19.89	4.53	800	765	5.4272	5.4276	+0.0004
77.39	21.84	0.77	75.53	23.63	0.84	830	603	5.4219	5.4218	-0.0001
76.52	17.41	6.07	74.57	18.80	6.63	700	800	5.4312	5.4313	+0.0001
73.70	23.91	2.39	71.63	25.76	2.60	800	450	5.4263	5.4263	0.0000
72.99	25.00	2.01	70.90	26.91	2.19	800	480	5.4260	5.4260	0.0000
72.75	26.14	1.12	70.65	28.13	1.22	800	765	5.4248	5.4246	-0.0002
71.30	28.31	0.39	69.15	30.43	0.42	830	603	5.4245	5.4240	-0.0005
66.62	19.07	4.31	74.69	20.60	4.71	830	603	5.4280	5.4282	+0.0002

tions, and that the following relation should hold

$$a = 5.4093 + 0.000456X + 0.00424Y + 0.00202Z, \text{ where } X, Y, \text{ and } Z$$

are the FeS, CdS, and MnS contents in mol per cent. To test the validity of this function three Fe- plus Mn- plus Cd-bearing sphalerites were prepared and measured. Results of the measurements are presented in Table 7, and show excellent agreement with the calculated cell edges.

Kullerud (1953) first suggested and demonstrated that the effects of Fe, Mn, and Cd on the cell edge of sphalerite were additive. He did not, however, obtain linear relations between cell edge and composition. The present work has shown that the binary, ternary, and quaternary relations are additive as well as linear. Although some of the present measurements are in disagreement with those of Kullerud, it is apparent that they amply substantiate his suggestion concerning the additivity of cell edges.

#### NATURAL SPHALERITES

Cell edges were carefully determined for nineteen analyzed sphalerites

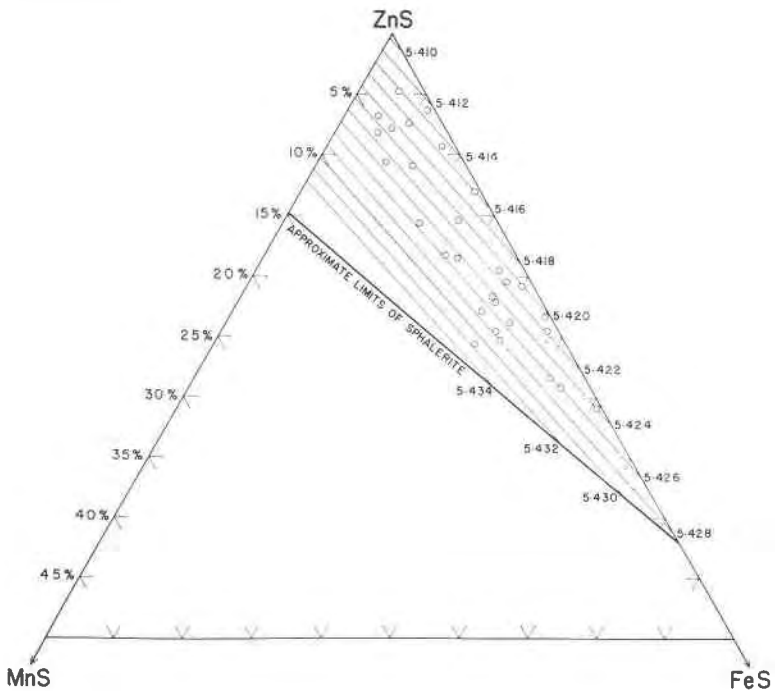


FIG. 2. Unit-cell edge (in Å) of synthetic sphalerite in the system ZnS-FeS-MnS. Compositions plotted in mol per cent. Approximate limits of sphalerite determined experimentally.



TABLE 6. UNIT-CELL EDGES OF Fe- PLUS Cd-BEARING SPHALERITES

Composition						Temp., ° C.	Time (hours)	Unit-cell edge, $a$ , Å		
Weight per cent			Mol per cent					Measured $\pm 0.0005$	Calculated	Difference
ZnS	FeS	CdS	ZnS	FeS	CdS					
94.72	4.37	0.91	94.55	4.84	0.61	765	750	5.4140	5.4141	+0.0001
92.51	4.80	2.69	92.84	5.34	1.82	765	750	5.4190	5.4194	+0.0004
90.27	8.51	1.22	89.90	9.38	0.82	765	750	5.4175	5.4171	-0.0004
86.94	10.03	3.03	86.85	11.11	2.04	765	750	5.4222	5.4230	+0.0008
86.45	4.97	8.58	88.44	5.64	5.92	765	750	5.4370	5.4370	0.0000
86.34	8.82	4.84	86.88	9.84	3.28	765	750	5.4275	5.4277	+0.0002
85.80	13.18	1.02	84.87	14.45	0.68	765	750	5.4188	5.4188	0.0000
84.69	12.65	2.48	84.39	13.94	1.66	765	750	5.4211	5.4227	+0.0016
81.64	10.20	8.16	82.93	11.48	5.59	800	360	5.4387	5.4382	-0.0005
80.69	16.65	2.66	79.94	18.28	1.78	765	750	5.4243	5.4251	+0.0008
80.25	15.32	4.43	80.08	16.94	2.98	765	750	5.4296	5.4296	0.0000
80.02	19.00	0.98	78.65	20.69	0.66	800	360	5.4212	5.4215	+0.0003
80.00	16.00	4.00	79.66	17.66	2.68	800	360	5.4289	5.4288	-0.0001
79.99	14.01	6.00	80.34	15.60	4.06	800	360	5.4333	5.4336	+0.0003
79.95	18.00	2.05	78.93	19.70	1.37	800	360	5.4239	5.4241	+0.0002
79.93	17.08	2.99	79.23	18.77	2.00	800	360	5.4267	5.4264	-0.0003
79.86	15.15	4.99	79.85	16.79	3.36	800	360	5.4312	5.4312	0.0000
79.25	19.81	0.94	77.82	21.56	0.62	765	750	5.4217	5.4217	0.0000
73.99	25.00	1.01	72.27	27.07	0.66	800	532	5.4250	5.4244	-0.0006
72.86	26.13	1.01	71.08	28.25	0.66	800	532	5.4242	5.4250	+0.0008
72.00	26.99	1.01	70.18	29.16	0.66	800	532	5.4256	5.4254	-0.0002
72.00	25.00	3.00	70.77	27.24	1.99	800	532	5.4300	5.4300	0.0000
71.77	22.12	6.11	71.48	24.42	4.10	800	789	5.4381	5.4378	-0.0003
71.00	28.00	1.00	69.13	30.22	0.65	800	532	5.4253	5.4259	+0.0006
70.89	22.11	7.00	70.81	24.48	4.71	800	789	5.4397	5.4405	+0.0008
70.01	29.00	0.99	68.09	31.26	0.65	800	532	5.4268	5.4264	-0.0004

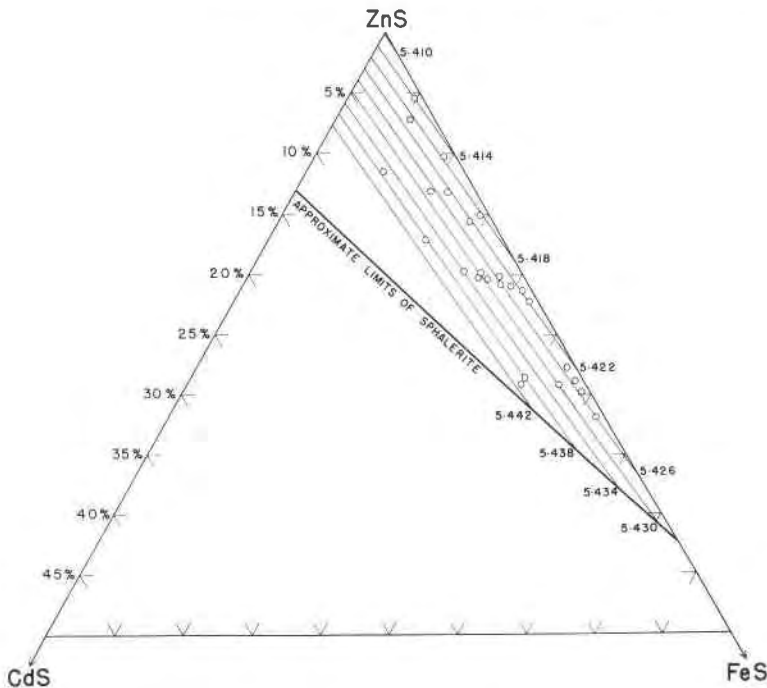


FIG. 3. Unit-cell edge (in Å) of synthetic sphalerite in the system ZnS-FeS-CdS. Compositions plotted in mol per cent. Approximate limits of sphalerite determined experimentally.

and the data compared with those for the synthetic compounds (Table 8). The sphalerites chosen cover a wide range of composition and were selected so that pure material could be hand-picked. Samples containing visible inclusions of other sulfide minerals were rejected. Polished section mounts were prepared of splits of all samples separated for analysis. Microscopic examination led to the rejection of various samples that showed exsolution bodies or intergrowths of other sulfide minerals. Any sample showing an obvious compositional zoning was also rejected, but it is realized that all of the samples undoubtedly contained some compositional inhomogeneities.

All samples were analyzed for their iron, manganese, cadmium, and copper contents. Zinc was not specifically determined in all samples, and

TABLE 7. COMPARISON OF MEASURED AND CALCULATED UNIT-CELL EDGES FOR Fe- PLUS Cd- PLUS Mn-BEARING SPHALERITES

Composition						Temp. ° C.	Time (hours)	Unit-cell edge, $a$ , Å		
Weight per cent			Mol per cent					Measured $\pm 0.0004$	Calculated	Difference
FeS	CdS	MnS	FeS	CdS	MnS					
5.15	1.43	2.26	5.68	0.96	2.53	850	350	5.4213	5.4211	-0.0002
8.88	1.44	1.37	9.78	0.97	1.52	850	350	5.4212	5.4210	-0.0002
18.02	1.04	2.20	19.60	0.69	2.42	750	450	5.4258	5.4260	+0.0002

where not determined was assumed to account for the remainder of the cations in the mineral. Sulfur was not determined in any sample and was assumed to be the only anion present. Natural sphalerites would not be expected to contain oxygen replacing the sulfur, although significant amounts of oxygen can be put into synthetic sphalerites (Skinner and Barton, 1960). In calculating the composition of the individual sphalerites in terms of the sulfide "molecule," any element present in amounts less than 0.1 per cent was ignored, and the totals adjusted to 100 per cent. This procedure is justified since compositional differences of less than 0.1 per cent cause changes in the cell edge less than the limit of error in the measurement of the cell edge.

The agreement between the measured and calculated cell edges is excellent; only two of the nineteen samples show differences between the calculated and measured  $a$  greater than the limit of measurement error in  $a$ . There is, however, a statistical preference for the calculated  $a$  to be slightly larger than the measured  $a$  (see Table 8). It is believed the reason for this lies in the difficulty of obtaining absolutely clean samples for analysis. Any slight amount of admixed impurity will of course contribute to the final analysis and accordingly be treated in calculation as if it were

TABLE 8.—COMPARISON OF CALCULATED AND MEASURED UNIT-CELL EDGES OF NATURAL SPHALERITES

	Composition										Unit-cell edge, $a$ , Å			Location
	Element, Weight per cent					Sulfide content, Mol per cent					Measured $\pm 0.0005$ Å	Calcu- lated	Differ- ence	
	Zn	Fe	Cd	Mn	Cu	ZnS	FeS	CdS	MnS					
1	N.D.	0.20	0.40	<0.01	<0.04	99.30	0.35	0.35	—	—	5.4106	5.4110	+0.0004	Joplin, Mo.
2	N.D.	0.30	0.41	<0.01	<0.05	99.12	0.52	0.36	—	—	5.4109	5.4110	+0.0001	Joplin, Mo.
3	N.D.	0.50	0.23	<0.01	<0.03	98.93	0.87	0.20	—	—	5.4099	5.4105	+0.0006	Belgium
4	N.D.	0.30	0.74	<0.01	<0.03	98.83	0.52	0.65	—	—	5.4121	5.4123	+0.0002	Hungary
5	N.D.	1.40	0.12	<0.01	<0.04	97.64	2.25	0.11	—	—	5.4110	5.4108	-0.0002	Waaroo, So. Australia
6	N.D.	5.10	0.42	<0.05	<0.04	90.84	8.84	0.36	—	—	5.4144	5.4148	+0.0004	Broken Hill, N.S.W.
7	N.D.	3.12	1.70	0.02	Tr.	93.04	5.45	1.48	—	—	5.4176	5.4181	+0.0005	Keystone, S. Dak.
8						88.31	10.97	0.72	—	—	5.4169	5.4174	+0.0005	Sevningdalen, Helgeland, Norway <sup>1</sup>
9						91.83	7.90	0.27	—	—	5.4131	5.4140	+0.0009	Breitenbrunn, Germany <sup>1</sup>
10	N.D.	7.20	0.22	1.40	0.05	84.97	12.39	0.19	2.45	—	5.4202	5.4206	+0.0004	Broken Hill, N.S.W.
11	56.2	7.60	0.22	1.37	<0.03	84.06	13.31	0.19	2.44	—	5.4215	5.4211	-0.0004	Broken Hill, N.S.W.
12	56.1	8.30	0.22	1.90	0.08	82.25	14.25	0.18	3.32	—	5.4230	5.4233	+0.0003	Broken Hill, N.S.W.
13	54.1	9.40	0.19	2.60	0.10	79.20	16.11	0.16	4.53	—	5.4260	5.4265	+0.0005	Broken Hill, N.S.W.
14	54.2	8.70	0.19	1.79	<0.03	81.35	15.29	0.17	3.20	—	5.4234	5.4235	+0.0001	Broken Hill, N.S.W.
15	N.D.	12.50	0.30	2.70	<0.01	74.30	20.87	0.25	4.58	—	5.4289	5.4292	+0.0003	Broken Hill, N.S.W.
16	56.72	8.10	0.25	1.50	<0.02	83.26	13.92	0.21	2.61	—	5.4220	5.4218	-0.0002	Zagoran, Mont.
17	53.54	12.50	0.14	0.21	<0.01	78.16	21.36	0.12	0.36	—	5.4197	5.4202	+0.0005	Cumberland, England
18	55.1	9.0	0.19	2.3	<0.03	80.5	15.3	0.16	4.0	—	5.4250	5.4251	+0.0001	Nairne, So. Australia <sup>2</sup>
19	55.0	8.8	0.18	2.5	<0.03	80.4	15.1	0.15	4.4	—	5.4242	5.4257	+0.0015	Nairne, So. Australia <sup>2</sup>

Analyses 1-6, 10-19, by Defense Standards Laboratories, Adelaide, South Australia.

Analysis 7 by Isidore Adler, U. S. Geological Survey.

<sup>1</sup> Analyses from Kullerud (1953), unit-cell edge measurements by Kullerud (personal communication).

<sup>2</sup> Skinner (1958).

in solid solution in the sphalerite. This will lead to too high a figure for the calculated  $a$ .

It can be concluded then, that the function relating the cell edges of synthetic sphalerites with their compositions also satisfactorily defines the relation for natural Fe- plus Mn- plus Cd-bearing sphalerites.

#### OTHER STUDIES

Bizouard and Roering (1958) measured the cell edge of an analyzed natural sphalerite and noted a large discrepancy between the observed and computed cell edges. The discrepancy becomes small when the data from the present study are used to compute the cell edge from the composition, although it would be necessary to measure the cell edge with greater precision to actually prove or disprove their point. They refer their measurements to a unit-cell versus composition curve determined by Henriques (1957). Henriques' data, however, do not show an internal consistency of measurement and are not determined with sufficient precision to allow adequate comparison with the present study.

Cell edge measurements of numerous analyzed sphalerites have been reported in the literature. Most of these studies, however, have limitations preventing reasonable comparison with the present work. Chudoba and Mackowsky (1939) found variations in the cell edges of natural sphalerites, but unfortunately their samples were only partially analyzed. Lazarenko (1955) states that he did not observe any change in the cell edge with changing composition. His measurements were insufficiently precise to record cell differences in the samples he studied, however, and his observations should be modified accordingly.

The suggestion has been made by Henriques (1957) that the thermal history of a sphalerite may affect the cell edge. Henriques apparently had a quenchable order-disorder effect in mind, because he draws an analogy to the feldspars. This is an inexact choice for an example; the mechanism of the complex order-disorder effects in the feldspar structures is not yet fully understood, and there is no evidence to suggest that such effects should or could occur in either natural or synthetic sphalerites. Some sphalerites may contain a certain amount of hexagonal close-packing (Smith, 1955), but this would not lead to the effects suggested by Henriques.

#### ACKNOWLEDGMENTS

This study was begun while the author was a member of the staff of the University of Adelaide, South Australia. The assistance of Robin Ofler in making certain of the unit-cell edge measurements is gratefully acknowledged. Brian Daly of the South Australian Museum and J. J.

Norton, U. S. Geological Survey, kindly loaned specimens for study. Gunnar Kullerud, Geophysical Laboratory, Carnegie Institution of Washington, generously allowed quotation of his unpublished measurements of the unit-cell edges of two analyzed sphalerites.

My colleagues Philip M. Betkhe and Paul B. Barton, Jr. have at all times been generous in their efforts and assistances.

## REFERENCES

1. BIRCH, FRANCIS, SCHAIRER, J. F., AND SPICER, H. C., 1942. Handbook of Physical Constants: *Geol. Soc. America Spec. Paper, No. 36*, 325 p.
2. BIZOUARD, H. AND ROERING, C., 1958, An investigation of sphalerite: *Geol. Foren. Stockholm Forh.*, **B 80**, 309-314.
3. BRAGG, W. L., 1947, The conversion factor for kX units to Ångstrom units: *Am. Mineral.*, **32**, 592.
4. CHUBODA, K. F. AND MACKOWSKY, M. T., 1939, Über die Isomorphie von Eisen und Zink in der Zinkblende: *Zentr. Mineral. Geol., Abt. A*, No. 1, 12-21.
5. GOLDSCHMIDT, V. M., 1927, Geochemische Verteilungsgesetze der Elemente VIII. Untersuchungen über Bau und Eigenschaften von Krystallen: *Skrifter Norsk. Vidensk. Akad. Oslo. I Mat. Natur. Klasse.* 1926, No. 8.
6. HENRIQUES, Å., 1957, Cell dimensions of sphalerite: *Arkiv. for Mineral. och Geol.*, **2**, p. 275.
7. KULLERUD, GUNNAR, 1953, The FeS-ZnS system. A geologic thermometer: *Norsk. geol. tidsskr.*, **32**, 61-147.
8. LAZARENKO, E. K., 1955, Blendes from pyritic deposits of the Middle Urals: *Sci. Annals Lvov State Univ., Ser. Geol.*, **35**, no. 8, 72-119.
9. SCHNASSE, H., 1932, Kristallstruktur der Manganosulfide und ihrer Mischkristalle mit Zinksulfid und Cadmiumsulfid: *Zeit. Physik. Chem. (B)* **20**, 89-117.
10. SKINNER, B. J., 1958, The geology and metamorphism of the Nairne Pyritic Formation, a sedimentary sulfide deposit in South Australia: *Econ. Geol.*, **53**, 546-562.
11. SKINNER, B. J. AND BARTON, P. B., JR., 1958, Recent work on sphalerite. Its bearing on the sphalerite geothermometer: (Abs.) *Geol. So. America Bull.*, **69**, 1768.
12. ———, 1960, The substitution of oxygen for sulfur in wurtzite and sphalerite: *Am. Mineral.*, **45**, 612-625.
13. SKINNER, B. J., BARTON, P. B., JR., AND KULLERUD, GUNNAR, 1959, Effect of FeS on the unit edge of sphalerite. A revision: *Econ. Geol.*, **54**, 1040-1046.
14. SMITH, F. G., 1955, Structure of zinc sulfide minerals: *Am. Mineral.*, **40**, 658-675.
15. TRAILL, R. J. AND BOYLE, R. W., 1955, Hawleyite, isometric cadmium sulfide, a new mineral: *Am. Mineral.*, **40**, 555-559.
16. ULRICH, F. AND ZACHARIASEN, W., 1925, Über die Kristallstruktur des  $\alpha$ - und  $\beta$ -CdS, sowie des Wurtzits: *Zeit. Krist.*, **62**, 260-273.

*Manuscript received January 17, 1961.*