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NEW WURTZITE POLYTYPES FROM JOPLIN, MISSOURI[*]

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Abstract

Small, hemimorphic hexagonal crystals implanted on botryoidal zinc sulfide from the Zig Zag Mine, Joplin, Missouri, have been studied by crystallographic and *x*-ray diffraction techniques. They are identified as a new wurtzite polytype, wurtzite-10H. The unit cell data are: space group, $P6_3mc$; $a=3.824$ Å, $c=31.20$ Å; cell contents, 10ZnS. Comparison of diffraction intensity data indicates that the published structure of SiC-10H (stacking sequence 3223) is different from that of wurtzite-10H. Calculation of intensities for various models shows that the stacking sequence for wurtzite-10H is 55. Crystals of wurtzite from Joplin described by A. F. Rogers (1904) were evidently wurtzite-10H. Powder diffraction data revealed the presence of another polytype, wurtzite-8H, with a hexagonal unit cell: space group $P6_3mc$; $a=3.82$ Å, $c=24.96$ Å; cell contents 8ZnS. Wurtzite-6H was also found at the Zig Zag Mine. The wurtzite polytypes evidently form a homologous series (2H, 4H, 6H, 8H, 10H) resulting from growth phenomena based on screw dislocations.

Occurrence

During the course of a study of the Zig Zag Mine in north Joplin, Missouri, by one of us (E.T.McK.), specimens of an unusual stalactite formation of zinc sulfide were collected. Optical examination of the radiating structure of these stalactitic forms in thin section showed that the mass consisted of about 90 per cent isotropic sphalerite and 10 per cent of an anisotropic zinc sulfide phase. On the surface of some of the stalactites small wurtzite-like pyramidal crystals were found implanted on their points, in a manner resembling prickly-pear fruit. This resemblance is most apt for the imperfect, rounded crystals which greatly outnumber those with well-defined crystal faces. As shown in the photograph in Fig. 1, a secondary crystal is occasionally found growing out of the base of the larger crystals. When clean, the crystals are brown to light brown, but their color is often obscured by a black stain covering the surface of the stalactites. None of them ranges over 2 mm. in size. These crystals have been proved by crystallographic and *x*-ray diffraction study to be a previously unreported polytype of wurtzite.

Crystallography

The crystal habit is characterized by a negative base and a steep positive pyramid. The faces of the best crystals gave poor signals on the goniometer, but good enough to indicate an inclination angle (ρ) of about $77\frac{1}{2}°$. This angle corresponds to the form $l\{50\bar{5}2\}$ as listed in Palache, Berman and Frondel (1944, p. 227). Frondel and Palache (1950) found in

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their study of the wurtzite polytypes from western Pennsylvania that the pyramidal form reflected the dimensions of the internal structure, but they report none having the form found on the Joplin crystals. It was suspected, therefore, that the Joplin wurtzite might constitute a new polytype, and this possibility was borne out by the x-ray study.

Buerger precession photographs were made of the $(h0.l)$ net in the hexagonal lattice. The resulting data for the Joplin wurtzite are given in Table 1. No polytype of zinc sulfide of these dimensions has been previously reported in either natural or artificial specimens (Frondel and Palache, 1950; Strock and Brophy, 1955). Also, the Joplin wurtzite, which in the notation of Frondel and Palache will be designated wurtzite-10H, constitutes the first natural occurrence of wurtzite polytypes outside of the western Pennsylvania (eastern Ohio) localities described by Seaman and Hamilton (1950). Table 2 compares the unit cell data for all the natural wurtzite polytypes, and shows that wurtzite-10H fits well in the series.

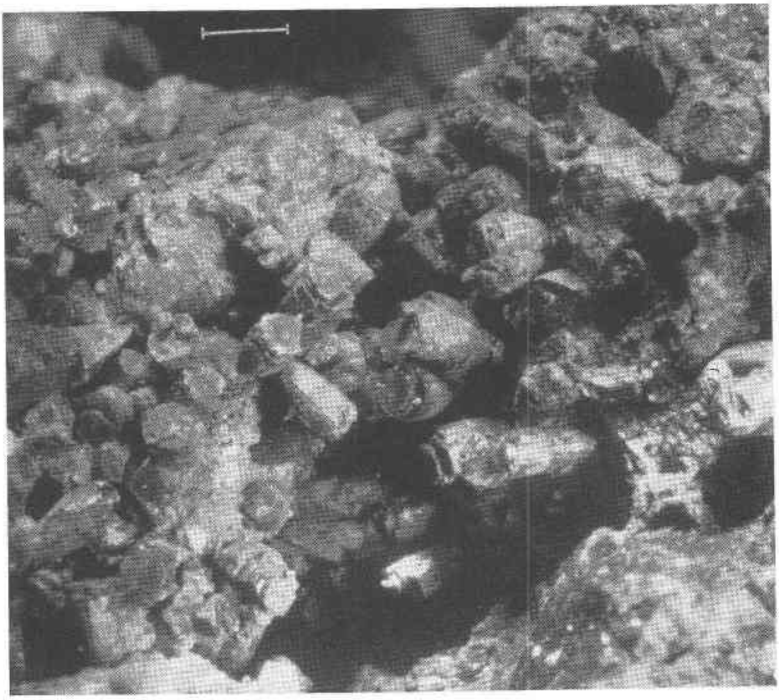


FIG. 1. Wurtzite-10H crystals in vug of botryoidal sphalerite from Zig Zag Mine, Joplin, Missouri. Bar at top indicates one mm. Photograph by J. A. Denson.

Among the abundant crystals of wurtzite-10H, crystals are sometimes found which have a somewhat more obtuse pyramid angle. Buerger precession photographs of one of these showed that they are wurtzite-6H, identical with that described by Frondel and Palache. The surfaces of these crystals were so poor that the crystal forms could not be identified, but they are characteristically more blunt in appearance than wurtzite-10H.

TABLE 1. CRYSTALLOGRAPHIC DATA FOR NEW WURTZITE POLYTYPES

Polytype:	8H	10H
Space group:	$P6_3mc$	$P6_3mc$
Cell constants:	$a = 3.82 \pm .01$ Å $c = 24.96 \pm .08$ Å $c/a = 6.53$ $p_0 = 7.53$	$a = 3.824 \pm .004$ Å $c = 31.20 \pm .03$ Å $c/a = 8.159$ $p_0 = 9.421$
Cell contents:	8ZnS ($Z=8$)	10ZnS ($Z=10$)
Forms:	—	$-c\{0001\}$ $l\{10\bar{1}2\}$ ($\rho = 78°01'$)
Structure parameters:	(provisional) $2Zn_1$ in (a), $z=0$ $2Zn_2$ in (b), $z=1/8$ $2Zn_3$ in (b), $z=3/8$ $2Zn_4$ in (b), $z=3/4$ S_1, S_2, S_3, S_4 corresponding to Zn atoms above, with $z_S = z_{Zn} + 3/32$	(established) $2Zn_1$ in (a), $z=0$ $2Zn_2$ in (a), $z=3/10$ $2Zn_3$ in (b), $z=1/10$ $2Zn_4$ in (b), $z=2/5$ $2Zn_5$ in (b), $z=7/10$ S_1, S_2, S_3, S_4, S_5 corresponding to Zn atoms above, with $z_S = z_{Zn} + 3/40$

The dark-stained, almost black stalactitic specimens appear to be coated with a late, very fine, crystalline deposit, possibly of sphalerite. Gently crushed crystal fragments of one of the wurzite polymorphs show under the microscope a fine banding of isotropic sphalerite parallel to the basal pinacoid. Precession photographs of crystals of wurtzite-6H taken from one of the coated stalactitic specimens show prominent but very diffuse spots corresponding to sphalerite, twinned on (111) and in oriented relation to the wurtzite-6H lattice. Photographs of clean, brown crystals of wurtzite-10H also show weaker sphalerite reflections. Consistent with optical observations, the x-ray patterns thus show the presence of sphalerite, either as an intergrown or alteration phase, or a surface coating, or both.

It should be noted that comparison of form symbols for the pyramidal forms is based on the dimensions of the unit cell assumed. Thus, $l\{10\bar{1}2\}$ for wurtzite-10H ($c:a=8.159$) is the same form (i.e., has the same ρ angle) as $l\{50\bar{5}2\}$ of wurtzite-2H ($c:a=1.6358$) and $l\{50\bar{5}1\}$ of A. F. Rogers ($c:a=0.8179$) (see below).

CRYSTAL STRUCTURE

Frondel and Palache (1950) found that the 4H, 6H, and 15R polytypes of wurtzite all had structures corresponding to previously known silicon carbide polytypes (Strukturbericht, 1931). It was natural, therefore, to compare the wurtzite-10H structure with that of silicon carbide-10H as described by Ramsdell and Kohn (1951). A close comparison of the diffraction intensities of the two crystals showed conclusively that the structures of ZnS-10H and SiC-10H are not the same.

There is a limited number of possibilities for different structures of a 10H polytype based on tetrahedral stacking sequences. The usual method of designating the stacking sequence consists of a series of digits, each digit representing the number of layers in an unbroken cubic sequence run, each run separated by a hexagonal layer shift (Ramsdell, 1947). Such a symbol will have an even number of digits which add up to the number of layers of tetrahedra in the repeat unit. The stacking symbols for the various wurtzite polytypes are given in Table 2. It can be shown that the only hexagonal sequences possible for wurtzite-10H, in either space group $P6_3mc$ or $P3m$, are:

55
82
4114
3223
7111
6121
5131
4312
212212
221122
311113
131131
321211
321112
21111112
11211211

Structure factor calculations show that the only sequence which at all accounts for the observed intensities is 55. In Fig. 2, the squares of the unitary structure factors for typical reflections are indicated. The apparent agreement is sufficient to prove the postulated stacking sequence. The structure may now be defined by the parameters given in Table 1. No attempt has been made to refine the structure of wurtzite-10H.

In the silicon carbide polytypes, the largest cubic run found in any case is 4 and most stacking sequences are combinations of 2 and 3

TABLE 2. UNIT CELL DATA FOR WURTZITE POLYTYPES

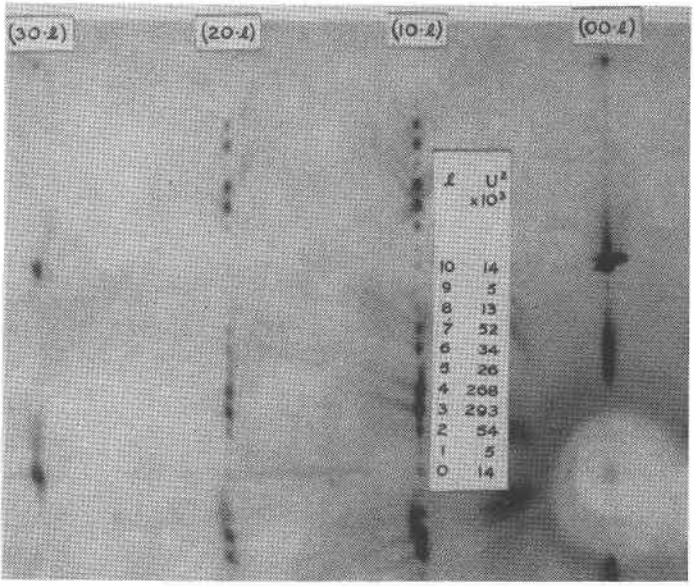
Data (except for 8H and 10H) from Frondel and Palache (1950)

Polytype Source	2H artificial	4H Pennsylvania	6H Pennsylvania, Missouri	8H Missouri	10H Missouri	15R Pennsylvania
Space group	$P6_3mc$	$P6_3mc$	$P6_3mc$	$P6_3mc$	$P6_3mc$	$R3m$
a, Å	3.819	3.814	3.821	3.82	3.824	3.830
c, Å	6.246	12.46	18.73	24.96	31.20	46.88
Z	2	4	6	8	10	15
c/Z, Å	3.123	3.116	3.121	3.12	3.120	3.126
Stacking	11	22	33	44	55	323232

(Structure Reports, 1951). For no really good reason, it has in the past been inferred from the known series of polytypes that the length of a cubic run in the ZnS and SiC polytypes is limited to 4 layers. Obviously, this assumption can no longer be held.

POWDER DIFFRACTION DATA

One of the brown crystals was gently crushed, without grinding, for making an x-ray powder diffraction photograph. The pattern strongly



ℓ	U^2 ×10^3
10	14
9	5
8	13
7	52
6	34
5	26
4	268
3	293
2	54
1	5
0	14

FIG. 2. Buerger precession photograph of ($h0l$) net of wurtzite-10H. Calculated values of the squares of the unitary structure factors (U^2, right column) agree well with photographic intensities.

resembles that of ordinary sphalerite, with the addition of many weak extra lines. The spacings observed are well accounted for by those predicted for wurtzite-10H, except for eight lines. Of these, one at 2.71 Å is associated with sphalerite, and indicates the presence of this mineral. The remaining seven could not be accounted for in terms of any of the postulated polytypes for which *d*-spacing data are given by Smith (1955) (2H, 4H, 6H, 9H, 15R, 21R).

On the assumption that the extra lines are produced by an unknown wurtzite polytype, an attempt was made to index them in terms of the single-layer hexagonal sub-cell with $a=3.824$ Å, $c'=3.120$ Å. The extra lines are all in the region where their indices would have the form $10.l'$, where l' will have fractional values depending on the number of layers in the polytype producing the lines. Then,

$$l' = \frac{\sqrt{1/d^2 - 0.09117}}{0.3205}.$$

For the seven lines the following results were obtained:

d	l'(obs)	l'(calc)	l
3.20	.251	.250	2
3.09	.363	.375	3
2.76	.625	.625	5
2.61	.736	.750	6
2.49	.826	.875	7
1.977	1.266	1.250	10
1.871	1.375	1.375	11

The comparison of the second and third columns leaves little doubt that the additional phase is an 8H polytype. Wurtzite-8H is therefore present with wurtzite-10H, and has a hexagonal unit cell with $c=24.96$, corresponding to 8 ZnS layers.

Complete data are given in Table 1. Wurtzite-8H is subordinate to wurtzite-10H in quantity, and is probably interlaminated with it. No evidence of the presence of wurtzite-8H could be seen on the single crystal photographs.

In Table 2 the observed powder data are compared with the calculated *d*-spacings for wurtzite-10H, wurtzite-8H and sphalerite. Below $d=1.600$ Å, only the sphalerite-like lines are indexed.

CHEMICAL COMPOSITION

The composition of the wurtzite-10H from the Zig Zag Mine was determined on two single crystals by I. Adler of the Geological Survey, using a micro-probe, spectrographic method (Alder and Axelrod, 1957). The analysis showed 1.4±0.2 wt. per cent Fe. No other metallic constit-

TABLE 3. INTERPRETATION OF *X*-RAY POWDER DIFFRACTION DATA FOR WURTZITE FROM JOPLIN, MISSOURI

CuKα radiation, camera diameter 114.6 mm.; film by M. E. Mrose

Joplin, observed		Wurtzite-10H		Wurtzite-8H		Sphalerite	
d(obs.)	Int.	*hk.l*	*d*(calc.)	*hk.l*	*d*(calc.)	*hk.l*	*d*(calc)
3.31	1	10.0	3.312	10.0	3.312		
		10.1	3.293				
				10.1	3.283		
3.26	6	10.2	3.240				
3.20	3			10.2	3.201		
3.16	2	10.3	3.156				
3.12	100	00.10	3.120	00.8	3.120	111	3.121
3.09	4			10.3	3.077		
3.05	4	10.4	3.049				
2.93	6	10.5	2.926	10.4	2.926		
2.81	1	10.6	2.794				
2.76	2			10.5	2.760		
2.71	3					200	2.705
2.66	1	10.7	2.659				
2.61	1			10.6	2.591		
2.52	1	10.8	2.525				
2.49	1			10.7	2.427		
		10.9	2.395				
		10.10	2.271	10.8	2.271		
		10.11	2.155				
				10.9	2.127		
2.08	2	10.12	2.045				
1.977	1			10.10	1.994		
1.937	1	10.13	1.944				
1.904	50	11.0	1.912	11.0	1.912	220	1.912
1.871	2			10.11	1.872		
1.841	1	10.14	1.849				
1.756	3	10.15	1.762	10.12	1.762		
1.678	1	10.16	1.681				
		20.0	1.656	20.0	1.656		
		20.1	1.654				
				20.1	1.652		
1.649	1	20.2	1.647				
				20.2	1.641		
		20.3	1.635				
1.626	35	11.10	1.630	11.8	1.630	311	1.631
				20.3	1.624		
		20.4	1.620				
1.598	1	20.5	1.601	20.4	1.601		
1.572	1						
1.558	1						
1.350	1					400	1.352
1.294	1						
1.239	4					331	1.240
1.207	1	11.20	1.209	11.16	1.209	420	1.209
1.168	1						
1.103	6	30.0	1.104	30.0	1.104	422	1.103
1.071	1						
1.039	4	30.10	1.041	30.8	1.041	511	1.040
		00.30	1.040	00.24	1.040		
.955	3	22.0	.958	22.0	.958	440	.956
.914	6	11.30	.914	11.24	.914	531	.914

uents were found within the range of the *x*-ray spectrograph. A chemical analysis of the massive zinc sulfide associated with wurtzite reported by Rogers (1904) gave 2.73 wt. per cent Fe. Mr. Adler also estimated Fe in a western Pennsylvania crystal at 3.7 wt. per cent, using the same microprobe technique.

EARLIER DESCRIPTION OF WURTZITE FROM JOPLIN

Wurtzite-10H, as described above, is probably the same as the wurtzite from Joplin described by A. F. Rogers (1904, p. 461–2). His crystals came from an abandoned mine in eastern Joplin. Rogers describes the occurrence of his crystals as follows:

> "Wurtzite occurs as small hemimorphic crystals, averaging about two mm. in length and one mm. in thickness in cavities in massive zinc sulfide (wurtzite?). One end of the crystal is terminated by the basal plane (pedion), while the other end, which is usually the one attached to the matrix, is terminated by the pyramid $l\{50\bar{5}1\}$ $5P$, · · · .
>
> "The massive zinc sulfide upon which the wurtzite crystals are implanted usually assumes a botryoidal, mammillary or stalactitic form."

He reports an inclination angle for the pyramid form of 78°5′, showing that the form of his crystals is identical with that of ours. Rogers' crystal drawings, reproduced in Fig. 3, serve to illustrate our crystals equally as well as his. There seems little doubt that the crystals that Rogers described were actually wurtzite-10H.

GENERAL OBSERVATIONS

The discovery of wurtzite-10H with stacking sequence 55 suggests the existence of a homologous series of polytypes: 2H, 4H, 6H and 10H, with stacking sequences 11, 22, 33 and 55 respectively. The presence of wurtzite-8H revealed by the powder diffraction patterns as described above provides a fifth member of this series. While the structure of wurtzite-8H has not been proved, there is good reason to believe that it

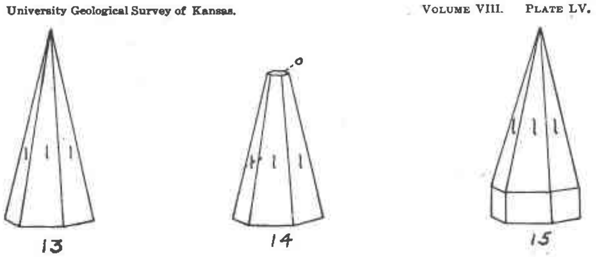


FIG. 3. Figures reproduced from Rogers (1904) which illustrate the crystal habit of wurtzite-10H showing $l\{10\bar{1}2\}$.

has the stacking sequence 44. This structure is the same as that of SiC-8H found by Ramsdell and Kohn (1952). It is understood that the polytypic structures may arise from accidents of spiral growth resulting from screw dislocations (Frank, 1951). This explanation is especially logical for the homologous series suggested here. The known members of the series evidently correspond to screw dislocations involving from 1 to 5 layers.

There are as yet no apparent clues as to what conditions of environment are responsible for the formation of wurtzite polytypes. While Smith (1955) has shown that incipient polytypism is present in all sphalerite and wurtzite crystals, only at Joplin and western Pennsylvania have homogeneous crystals of individual polytypes been found. About the only features in common to the wurtzite genesis at the two localities is that the crystals were apparently formed from mineralizing solutions (low in iron) at low temperatures ($<100°C$). While some polytypes have been found at only one locality, there is no reason to suppose that these and other polytypes should not be found eventually in many places. The presence of the homologous series at both the known localities indicates that the same growth phenomena prevail in both environments.

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