X-RAY MEASUREMENTS ON ARGENTOPYRITE

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ABSTRACT

New observations on argentopyrite from Freiberg and Joachimstal lead to the following data for the species:

Orthorhombic, probable space group D_{2h}^{13}—*Pmmn;* unit cell with $a=6.64$, $b=11.47$, $c=6.45$ Å and $a:b:c=0.5789:1:0.5623$, contains $4[AgFe_2S_3]$; specific gravity, 4.25 (meas.) 4.27 (calc.). The crystals are markedly pseudohexagonal due to interpenetrating twinning; lamellar twinning is also present. Crystals display the forms b {010}, m {110}, n {120} x {011} and c {001}, the termination faces are usually rough. The x-ray powder diffraction data index completely with the lattice dimensions.

Argentopyrite is classified in Dana's System of Mineralogy (1944) as an incompletely described mineral, possibly dimorphous with sternbergite ($AgFe_2S_3$). The prismatic six-sided twinned crystals of argentopyrite were originally described as monoclinic. Schrauf (1871) showed that the mineral is orthorhombic and pseudohexagonal by twinning. Weisbach (1877) described brittle, apparently hexagonal prismatic crystals from Marienberg which are clearly argentopyrite but differ in specific gravity from the original material. Weisbach also described "argyropyrite" as non-brittle pseudohexagonal twinned crystals with a perfect basal cleavage from Himmelsfurst mine, Freiberg. Streng (1878) described crystals of "Silberkies" from Andreasberg which are pseudohexagonal twins, and similar in silver content and specific gravity to Weisbach's material from Marienberg. In connection with a study of frieseite the late Professor M. A. Peacock also made some observations on a specimen of argentopyrite (87701) from the Holden Collection of Harvard University. Peacock (1942) published his observations on frieseite together with new data on sternbergite in a brief abstract; his observations on argentopyrite remain unpublished. The present report combines these unpublished observations with new data obtained from other specimens of this mineral.

The specimens which we have studied are from Freiberg and Joachimstal, one (Freiberg) supplied by Ward's Natural Science Establishment, one from the Royal Ontario Museum (M13001) and one from the National Museum at Washington (R541). The specimen from Ward's carries a crust of prismatic crystals of argentopyrite, practically all tarnished iridescent or blackened. These crystals appear as simple hexagonal prisms (even those appearing most perfect have striations on the faces of the prism zone), or as more or less deeply grooved prisms with reentrant angles sharply marked. Most show no definite terminations, but some show a low pyramidal development, sometimes six more or less imperfect faces, at other times fewer which are recognizable. Even the best of these, when examined on the reflecting goniometer, give very poor signals. The average rho angle for these is close to 29°, representing, as will be shown later, (011) faces. A considerable number, particularly of the larger individuals, show an irregular core of foreign material, slightly harder than argentopyrite. Polished sections, made perpendicular to the prism show this core to be isotropic. Micro-chemical reactions indicate

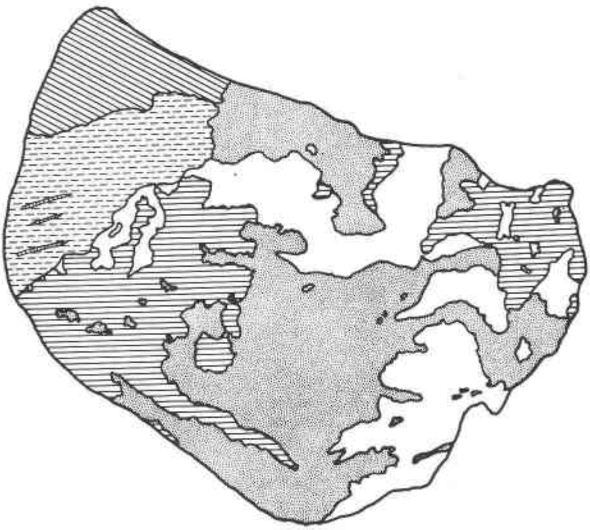

FIG. 1. Argentopyrite; polished section on (001) in polarized light with crossed nicols. Intricate interpenetration twinning shown by the distribution of patterns. Each pattern represents an individual.

silver and iron, but the amount is too small for further identification to be possible. Associated minerals are gypsum, appearing in tiny water clear crystals perched on a crust of argentopyrite and other minerals, and dull gray, botryoidal crusts of arsenic (identified from x-ray powder pattern). Some proustite and occasional grains of pyrite, and possible other sulphide minerals were observed.

Polished surfaces were made of some of the larger individuals, normal to the prism zone. These show in polarized light under crossed nicols an extremely intricate intergrowth of numerous individuals, revealed by rather intense interference colors, ranging from very deep blue through paler shades of blue gray, to bright grayish white which is the color in ordinary light. The very strong anisotropism in this orientation, and the presence of intergrowths, further confirm the non-hexagonal character of the mineral. The complexity of intergrowth is not confined to the basal plane, as one crystal, mounted with a prismatic (probably 010) face in reflecting position showed equal irregularity of grain shape as well as occasional lamellae with trace of plane parallel to *c*. Some idea of the complexity of these intergrowths is indicated in the accompanying drawing (Figure 1) made from observations of a specimen in polarized light with crossed nicols.

The Royal Ontario Museum specimen (Joachimstal) also showed rather brightly tarnished crystals, but in some areas the argentopyrite was essentially fresh, bronze brown in color, and giving excellent reflection signals from prism zone faces. Even here, the terminal faces were poor in quality. Few or no cored individuals were noted on this specimen. Earlier than argentopyrite, dull gray rosette-like cubic crystal aggregates of chloanthite are abundant. This mineral also was identified by its *x*-ray powder pattern and micro-chemical tests for nickel and arsenic, cobalt was absent. Considerable associated proustite was noted in the specimen.

On the National Museum specimen the crystals of argentopyrite are sharp hexagonal prisms, rarely striated parallel to *c* and with a low roughly pyramidal termination. The crystals are tarnished, green, blue, yellow and purple. The crust of argentopyrite is underlain by ruby silver, and rhombohedrons of siderite are also present.

Geometrical Crystallography

M. A. Peacock measured 2 crystals of argentopyrite from Joachimstal, leaving sketches and measurements of these crystals. One crystal is a psuedohexagonal twin showing the form {010} represented by 5 large faces (Figure 2), the form {120} with 2 faces bevelling each (010) face. Adjacent (120) faces of different individuals meet in a deep re-entrant notch. Narrow re-entrant grooves formed by two (120) faces also occur in two of the (010) faces. The crystal is terminated by six faces of the form {011} and a rough face approximating the basal pinacoid. Peacock's second crystal is much more complex showing pseudohexagonal twinning and fine lamellar twinning. A third small crystal, apparently a simple hexagonal prism (0.5×0.1 mm.), was selected for *x*-ray measurements.

Some interfacial angles from the literature are shown in Table 1 in comparison with measured angles from Peacock's notes and our recent measurements. Schrauf's (1871) elements fit the measured angles fairly well. Schrauf's observed form *n*{130} becomes {310} in the present setting although erroneously written as {130} in Dana (1892). It is worth noting that the angle $110\wedge310$ is very close to the angle $110\wedge120$

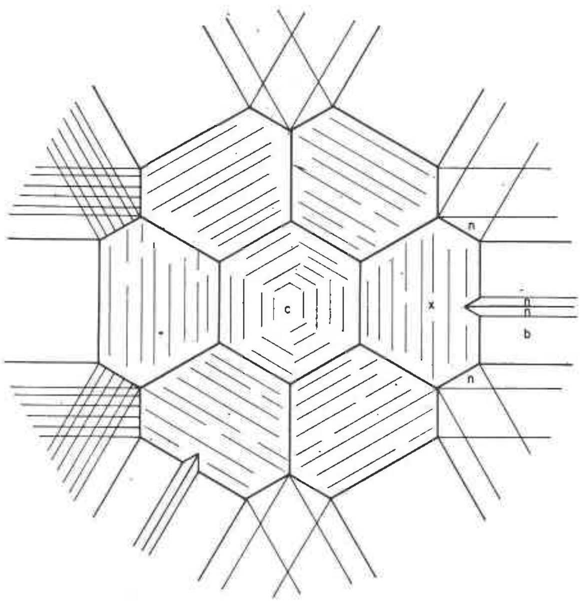

FIG. 2. Idealized drawing, from a working sketch by M. A. Peacock, of a twinned crystal of argentopyrite from Joachimstal showing faces of *c*{001} rough, *x*{011} striated parallel to edge with *b*(010); *b*{010} and *n*{120} folded into the plane of the drawing along the intersection with faces of *x*{011}. Faces of *n*{120} often form grooves on (100), some (120) faces are striated vertically.

(Table 1). Peacocks' crystal (Figure 2) clearly shows two faces (120) adjoining each of the five (010) faces on each side at polar angles of about 40°. In this case the indexing is established without ambiguity. It is probable then that Schrauf's *n*{310} is really {120}. Murdoch's more complex crystal shows polar angles in the prism zone of about 40° which requires that some faces be indexed (120). Streng (1878) records the face (130) which we have not seen on our crystals. The *c* length in Schrauf's axial ratio has been doubled and the one terminal face which is well established has here been indexed (011), in keeping with the structural lattice described in the next section.

STRUCTURAL CRYSTALLOGRAPHY

Small six-sided prismatic crystals of argentopyrite suitable for single crystal *x*-ray studies were readily available on the museum specimens of this mineral. M. A. Peacock, in 1940, made rotation and Weissenberg films on a small crystal from Joachimstal. Specimens from Joachimstal (U.S.N.M. R541, labelled "frieseite"), (R.O.M. M13001) and Freiberg

TABLE 1. ARGENTOPYRITE: CRYSTAL MEASUREMENTS
$a:b:c=0.5812:1:0.5498$ (Schrauf, 1871)

		Observed			Calculated
		Average	Range	Obs.	
Joachimstal (Schrauf, 1871)	010∧110		59°30′–59°52′		59°50′
	010∧010 tw.		60 10 –60 30		60 20
	110∧310		19 05 –19 30		19 12½
	110∧120				19 07
	010∧011		60 40 –61 12		61 12
	110∧112		61 20		61 15
Andreasberg (Streng, 1878)	010∧010 tw.		59 45 –60 50		{59 20 / 60 20
	010∧130		29 29 –31 09		29 50
	010∧011		57 36		61 12
Joachimstal (M. A. Peacock)	010∧110	58°45′	58 –59 30	(2)	59 50
	010∧010 tw.	{59 36	59 31 –59 41	(2)	59 20
		60 13	59 57 –50 43	(4)	60 20
	010∧120	40 30	38 44 –40 35	(7)	40 43
	010∧011	01 03	60 15 –62 11	(9)	61 12
Freiberg (J. M.)	010∧010 tw.	{58 47	57 41 –59 52	(2)	59 20
		60 38	60 02 –61 25	(4)	60 20
	010∧120	40 31	40 04 –40 50	(6)	40 43
Joachimstal (J. M.)	010∧011		60 30 –63 00	(5)	61 12

(U.C.L.A.) also yielded crystals suitable for single crystal measurements.

The single crystal x-ray films yield the lattice dimensions given in Table 2. The Weissenberg films with iron radiation show almost perfect hexagonal symmetry with $h00$, $h01$, etc., indistinguishable from $h\cdot 3h\cdot 0$, $h\cdot 3h\cdot 1$, etc., and $hh0$, $hh1$, etc., indistinguishable from $0k0$, $0k1$, etc. The high order reflections $6003 \simeq 90$ and $330 \simeq 060$ are split into two spots on most films with iron radiation but it is not possible to index these points correctly unless we assume that the $a:b$ ratio is greater than 0.5773:1 $(1:\sqrt{3})$. On Peacock's films (CuK radiation), which have more reflections in the high θ region, there is a visible lack of symmetry in the intensities of the high order reflections on either side of $hh0$ and $h\cdot 3h\cdot 0$ while symmetry is present on either side of $h00$ and $0k0$. This demon-

TABLE 2. ARGENTOPYRITE: LATTICE DIMENSIONS[1]

	a	b	c	Observer	Radiation
Joachimstal (H.M.M. 87701)	6.65 Å 0.5813	11.44 Å 1	6.43 Å 0.5620	Peacock	CuK
Joachimstal (U.S.N.M. R541)	6.63 0.5775	11.48 1	6.45 0.5618	L.G.B.	FeK MoK
Joachimstal (R.O.M. M13001)			6.44	J.M.	Fe$K\alpha$
Freiberg (U.C.L.A.)	6.63 0.5775	11.48 1	6.46 0.5627	J.M.	Fe$K\alpha$
Freiberg (from powder pattern)	6.64 0.5784	11.48 1	6.47 0.5636	J.M. & L.G.B.	Fe$K\alpha$
Average	6.64 0.5789	11.47 1	6.45 0.5623		
Axial ratio	0.5812	1	0.5498	Schrauf (1871)	

[1] Using Mo$K\alpha$ 0.7107; Cu$K\alpha$ 1.5418; Fe$K\alpha$ 1.9373.

strates clearly that the lattice is not hexagonal either in symmetry or dimension. Peacock's cell dimensions have an $a:b$ ratio which differs significantly from $1:\sqrt{3}$ and agrees closely with the morphological $a:b$ ratio. The morphological $b:c$ ratio, which is based on rather poor observations of one form only, agrees rather poorly with the x-ray measurements. The x-ray powder lines which index as pinacoid reflections (Table 4) lead to the dimensions given in Table 2, line 8. The average cell dimensions then are

$$a=6.64,\ b=11.47,\ c=6.45\ \text{Å}$$

These dimensions are used to index the powder pattern given later in Table 4.

The Weissenberg films about the c axis give the pattern shown in lower part of Figure 3. The solid circles appear on the zero layer and all points shown, in general, appear on the upper layers. Indexing in the normal way would require doubling all the h and k indices shown, in order to give rational indices to the points not indexed. We know however that crystals of argentopyrite show complex pseudohexagonal twinning. If we apply the operations of this type of twinning to the indexed points of the reciprocal lattice in Figure 3 the open circle points with $h+k=2n+1$

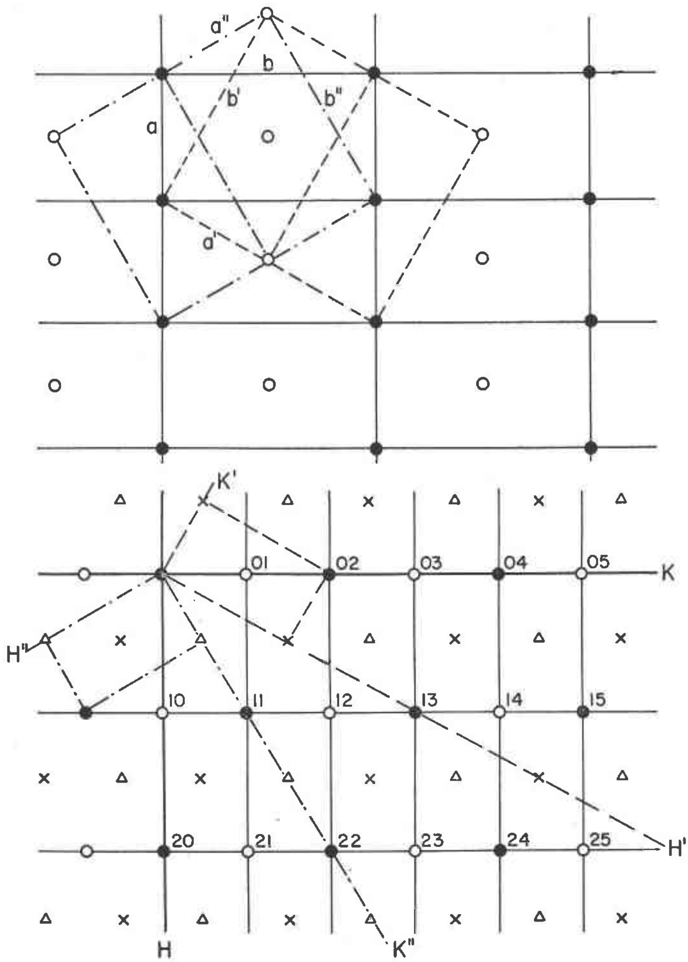

FIG. 3. Upper; plan of direct lattice of argentopyrite perpendicular to c, with $a=6.64$, $b=11.47$ Å; $a'b'$ and $a''b''$ direct lattice in twinned position by rotation of ab about $[1\bar{1}0]$ and[110].

Lower; reciprocal lattice projection of Weissenberg films. Solid points appear on zero layer (except origin); all points in general, appear on upper layers. Twinning by rotation about $[1\bar{1}0]$ brings the open circles into the X positions with axial directions $H'K'$ and about [110] brings the open circles into the Δ positions with axial directions $H''K''$; these axial directions are the reciprocal lattice axes corresponding to the direct lattice in twinned position $a'b'$ and $a''b''$.

fall on the points marked with triangles and crosses, and the solid points are common to all three orientations (indicated by HK; $H'K'$ and $H''K''$). Therefore all observed diffractions can be indexed in terms of a cell with the dimensions given above.

A rotation film, taken on a crystal rotating about the *b* axis (the normal to one of the large prism faces) shows strong zero and sixth layer lines and weak first to fifth, seventh and eighth layer lines. This rotation film leads to a period of 22.97 Å, double the *b*-period given above. Considering the twinning however, this axis of rotation is the *b* axis in one individual and the axes [310] and [$\bar{3}$10] in the two twinned individuals, furthermore it will be seen in Figure 3 that the odd layer lines will be made up of reciprocal lattice points from the two twinned lattices. In the direct lattice drawing it is obvious that the period [310]$\simeq$2*b*.

The observed diffractions for the untwinned cell are: *hkl*, all present; *hk*0 present only with *h* and *k* even; 00*l* present only with *l* even; these are characteristic of the space group D_{2h}^{13}—*Pmmn*. This is the probable space group if the crystals are holohedral.

Specific Gravity and Composition

The early descriptions of argentopyrite give specific gravity determinations which fall in three distinct ranges. The variety "argyropyrite" was distinguished from argentopyrite partly by the specific gravity. Some of the published values are given below, along with new unpublished determinations made by Dr. F. G. Smith with a Berman balance at the University of Toronto in 1940–41.

Argentopyrite		
Joachimstal	6.47	von Waltershausen (in Dana, 1944)
	5.33	Schrauf (1871)
Marienberg	4.06–4.12	Weisbach (1877)
Andreasberg	4.18	Streng (1878)
"Argyropyrite"		
Freiberg	4.206	Weisbach (1878), with cleavage (001)
Argentopyrite		
Andreasberg		
(H.M.M. 81808)	4.23	F. G. Smith
(U.T. 592)	4.26, 4.27	F. G. Smith
Himmelsfurst, Freiberg		
(H.M.M. 81792)	4.19	F. G. Smith
Joachimstal		
(H.M.M. 81807)	4.03	F. G. Smith
no locality	4.13	F. G. Smith
	4.14	F. G. Smith
	4.25	F. G. Smith

From this tabulation it appears that the early high values of von Waltershausen and Schrauf are in error, since no likely minerals have high enough specific gravity to affect the determination materially. A value

TABLE 3. ARGENTOPYRITE: ANALYSES AND UNIT CELL CONTENTS ($M=1257$)

	Joachimstal (von Waltershausen, 1866)				*Andreasberg (Streng, 1878)*			
	1	2	3	4	5	6	7	8
Ag	26.50	3.09	3	26.72	32.89	3.84	4	34.17
Fe	39.30	8.84	9	41.51	35.89	8.10	8	35.37
S	[34.20]	13.41	12	31.77	30.71	12.07	12	30.46
Total	100.00			100.00	99.74			100.00
G	6.47?		4.09		4.18		4.27	

1,5. Analyses. 2,6. Unit cell content for cell with $a=6.64$, $b=11.47$, $c=6.45$ Å and G $=4.25$. 3,7. Idealized cell content with calculated specific gravity. 4. Composition for $3[AgFe_3S_4]$. 8. Composition for $4[AgFe_2S_3]$.

of 4.25 appears closely to represent the specific gravity of argentopyrite. The analyses of argentopyrite also show considerable variation. One complete analysis and one partial analysis are given in Table 3 together with the unit cell contents, using the measured specific gravity of 4.25. Single silver determinations of 22.3 per cent (Schrauf 1871) and 28.8 per cent (Weisbach 1877) also appear in the literature. The analysis of argyropyrite (Weisbach 1877) is similar but we have no new observations that will help settle the status of this material. In considering the unit cell content we are inclined to give most weight to the complete analysis by Streng; indeed the numbers of atoms obtained from this analysis appear most reasonable. This cell content $4[AgFe_2S_3]$ leads to a calculated specific gravity 4.27 in close agreement with the measured values, and is more in keeping with the atomic positions in the space group if the structure is centrosymmetrical. The cell content given by the older and incomplete analysis (von Waltershausen, 1866) gives poor agreement between the measured and calculated specific gravity and includes odd numbers of silver and iron atoms. In preparing material for analysis it would be almost impossible to be certain of the absence of pyrite or marcasite and analyses are very likely to be low in silver. The silver minerals which have been reported in association with argentopyrite would be more readily removed in purification and if present should supply additional elements to the analysis.

The most likely cell content for argentopyrite, $4[AgFe_2S_3]$ supports the suggestion that this mineral is dimorphous with sternbergite $8[AgFe_2S_3]$. It is then possible that argyropyrite is a paramorph of sternbergite after argentopyrite. There is a close similarity between the cell dimensions of argentopyrite and sternbergite.

TABLE 4. ARGENTOPYRITE—$AgFe_2S_3$: X-RAY POWDER PATTERN[1]
Orthorhombic *Pmma*; $a=6.64$, $b=11.47$, $c=6.45$ Å, $Z=4$

I(Fe)	d(meas)	hkl	d(calc)
3	5.81 Å	110	5.747 Å
		020	5.735
½	5.68	011	5.622
2	4.67	101	4.627
2	4.30	111	4.291
		021	4.283
5	3.624	121	3.600
10	3.341	200	3.320
		130	3.313
10	3.318	031	3.289
1	3.226	002	3.225
4	3.110	012	3.104
1	2.962	201	2.952
		131	2.947
3	2.902	102	2.901
3	2.878	220	2.873
		040	2.867
½	2.816	112	2.812
		022	2.810
1	2.633	221	2.624
		041	2.620
2	2.591	122	2.588
½	2.523	032	2.465
3	2.434	141	2.437
1	2.323	231	2.337
1	2.276	212	2.268
1	2.178	310	2.173
		240	2.170
		150	2.168
		051	2.161
1	2.120	013	2.113
½	2.040	103	2.045
		142	2.039
½	2.017	113	2.014
		023	2.013
1	1.988	232	1.979
5	1.931	123	1.926
4	1.908	060	1.912
		330	1.915
½	1.869	052	1.869
7	1.808	251	1.811
		203	1.804
		133	1.803
1	1.749	322	1.738
1	1.673	143	1.665
1	1.660	400	1.660
		260	1.657
1	1.613	004	1.612
1	1.597	162	1.596
1	1.544	421	1.548
		351	1.546
		171	1.544
		303	1.542
1	1.458 Å	072	1.461 Å
½	1.450	204	1.450
		134	1.450
½	1.436	214	1.439
		271	1.432
½	1.429	333	1.430
		063	1.428
		422	1.429
		352	1.428
		172	1.427
½	1.383	144	1.375
½	1.366	181	1.369
2	1.321	054	1.319
		510	1.319
		370	1.317
		280	1.316
2	1.311	403	1.314
		263	1.312
½	1.264	105	1.266
		025	1.258
		115	1.258
1	1.236	125	1.236
		334	1.233
		064	1.232
2	1.203	205	1.202
		135	1.202
		363	1.200
½	1.156	404	1.156
		264	1.156
½	1.135	451	1.140
½	1.126	503	1.130
1		292	1.116
1	1.118	305	1.114
		1.10.1	1.113
		523	1.108
1	1.107	434	1.107
		600	1.107
		390	1.104
1	1.090	601	1.091
		391	1.088
1	1.081	533	1.084
		453	1.083
		193	1.082
		006	1.075
½	1.043	602	1.046
		392	1.045
		612	1.043
½	1.019	514	1.021
		374	1.020
		284	1.020

[1] Using $FeK\alpha$ 1.9373 (manganese filter) and a 114.59 mm. diameter powder camera.

sternbergite *Cmma* $a=6.63$, $b=11.60$, $c=12.68$ Å Peacock (1941)
argentopyrite *Pmmn* $a=6.64$, $b=11.47$, $c=6.45$ Å

X-RAY POWDER PATTERN

The x-ray powder pattern data for argentopyrite are listed in Table 4 together with the indices and spacings calculated from the lattice dimensions. The patterns for crystal powders from different specimens show a few weak lines which do not appear on all patterns. These lines compare closely in spacing with the strong lines of arsenic, argyrodite, marcasite and smaltite (chloanthite) and have been omitted from the data in Table 4. Some of M. A. Peacock's powder films of materials from the Harvard Museum show strong pyrite lines.

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