Zeitschrift für Kristallographie, Bd. 110, S. 136—144 (1958)

The Crystallography of Silver Sulfide, Ag_2S

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With 5 figures

(Received October 25, 1957)

Auszug

An einem Kristall von Akanthit (β-Ag_2S) von Freiberg i. Sa. wurde die Raumgruppe $P2_1/n$ bestimmt; die Gitterkonstanten sind $a = 4{,}23$ Å, $b = 6{,}91$ Å, $c = 7{,}87$ Å, $\beta = 99°35'$. Die Elementarzelle enthält 4 Ag_2S. Alle Atome nehmen allgemeine Punktlagen ein mit Ag(I) in $x = 0{,}758$, $y = 0{,}015$, $z = 0{,}305$; Ag(II) in $x = 0{,}285$, $y = 0{,}320$, $z = 0{,}435$ und S in $x = 0{,}359$, $y = 0{,}239$, $z = 0{,}134$.

Akanthit hat wie auch der Argentit (α-Ag_2S) ein raumzentriertes Gitter; die Atomanordnung ist jedoch bei beiden ganz verschieden. Das durch Abkühlen aus α-Ag_2S entstehende β-Ag_2S setzt sich aus kleinen Bereichen zusammen, in denen eine der Richtungen $[10\bar{3}]^*$, $[121]^*$ und $[\bar{1}21]^*$ eines Bereichs parallel einer der beiden anderen Richtungen benachbarter Bereiche verläuft.

Abstract

The space group of a single crystal of naturally occurring acanthite (β-Ag_2S) from Freiberg, Saxony, was found to be monoclinic $P2_1/n$; the cell constants were determined as $a = 4.23$ Å, $b = 6.91$ Å, $c = 7.87$ Å, $\beta = 99°35'$. There are 4 (Ag_2S) per unit cell and all atoms lie on the following fourfold general positions. Ag(I): $x = 0.758$, $y = 0.015$, $z = 0.305$; Ag(II): $x = 0.285$, $y = 0.320$, $z = 0.435$; and S at $x = 0.359$, $y = 0.239$, $z = 0.134$.

Acanthite has, in common with argentite (α-Ag_2S), a body-centered cubic arrangement of the sulfur atoms, although the arrangement of the silver atoms in the two polymorphs is quite different. When crystals are cooled from α to β, the crystals of β contain many small domains related to each other in orientation by having the directions $[10\bar{3}]^*$, $[121]^*$ and $[\bar{1}21]^*$ in one domain parallel to other combinations of these directions in the other domains.

Introduction

At room temperature silver sulfide forms monoclinic crystals known to mineralogists as acanthite. The crystallography of this phase has been much discussed in the literature, the most recent and comprehensive study being that of RAMSDELL[1]. However, no complete structure determination has been attempted.

Above 173 °C the stable phase of silver sulfide (α-Ag_2S) is body-centered cubic. The mineralogists have labeled as argentite those crystals having cubic morphology, although the cubic structure is never retained at room temperature, and these specimens are actually acanthite pseudomorphic after argentite. The structure of the α phase was determined by RAHLFS[2] from four lines on a powder photograph taken at 250 °C. It was described as a structure in which the sulfur atoms occupy the corners and center ($0\,0\,0;\ \frac{1}{2}\,\frac{1}{2}\,\frac{1}{2}$) of a 4.88 Å cubic cell, and in which the silver atoms are statistically distributed in the following 42 positions:

$$
\begin{array}{lllll}
 & (0\,0\,0;\ \frac{1}{2}\,\frac{1}{2}\,\frac{1}{2})\ + & & & \\
6\,(b) & \frac{1}{2}\,0\,0 & 0\,\frac{1}{2}\,0 & 0\,0\,\frac{1}{2} & \\
12\,(d) & \frac{1}{2}\,0\,\frac{1}{4} & \frac{1}{4}\,\frac{1}{2}\,0 & 0\,\frac{1}{4}\,\frac{1}{2} & \\
 & \frac{1}{2}\,0\,\frac{3}{4} & \frac{3}{4}\,\frac{1}{2}\,0 & 0\,\frac{3}{4}\,\frac{1}{2} & \\
24\,(h) & u\,u\,0 & u\,\overline{u}\,0 & \overline{u}\,u\,0 & \overline{u}\,\overline{u}\,0 \\
 & u\,0\,u & \overline{u}\,0\,u & u\,0\,\overline{u} & \overline{u}\,0\,\overline{u} \\
 & 0\,u\,u & 0\,u\,\overline{u} & 0\,\overline{u}\,u & 0\,\overline{u}\,\overline{u}
\end{array}
$$

where $u = 5/8$.

The structure of acanthite

RAMSDELL determined the cell constants as follows[1]:

$$a = 9.47\ \text{Å},\quad b = 6.92\ \text{Å},\quad c = 8.28\ \text{Å},\quad \beta = 124°.$$

The space group symmetry was determined as $B\,2_1/c$ (C_{2h}^5). With the density of 7.22 the cell contains 8 Ag_2S. Although this orientation of the cell may have certain advantages, especially in describing the twinning, the adoption of a primitive cell related to RAMSDELL's cell by $\frac{1}{2}\,0\,\frac{1}{2}/0\ 1\ 0/\frac{1}{2}\ 0\ \bar{\frac{1}{2}}$ is to be preferred. The cell constants for this new orientation were redetermined from a sample of acanthite from Freiberg, Saxony (Harvard University Museum No. 81814) by the BUERGER precession technique using Mo$K\alpha$ = 0.710 Å as follows:

$$a = 4.23\ \text{Å},\quad b = 6.91,\quad c = 7.87,\quad \beta = 99°35'.$$

[1] L. S. RAMSDELL, The crystallography of acanthite, Ag_2S. Amer. Mineralogist **28** (1943) 401–425.

[2] P. RAHLFS, Über die kubischen Hochtemperaturmodifikationen der Sulfide, Selenide und Telluride des Silbers und des einwertigen Kupfers. Z. physik. Chem. B **31** (1936) 157–194.

The space group in the new orientation is $P2_1/n$, and with a cell volume of 226.8 Å^3 the cell contains 4 Ag_2S.

To obtain a single crystal for the purposes of determining intensities, it was necessary to fracture a small twinned Freiberg crystal at liquid-nitrogen temperature. The best tiny fragment chosen had but a trace of an unoriented crystal on it and was highly irregular in shape. This gave rise to strong anisotropic absorption for which no correction could be easily made. Intensity data for the *a* axis, zero, first, second and third levels were gathered by an equi-inclination GEIGER-counter spectrometer using Cu$K\alpha$ radiation. The data were corrected for LORENTZ and polarization factors by the accepted method[3].

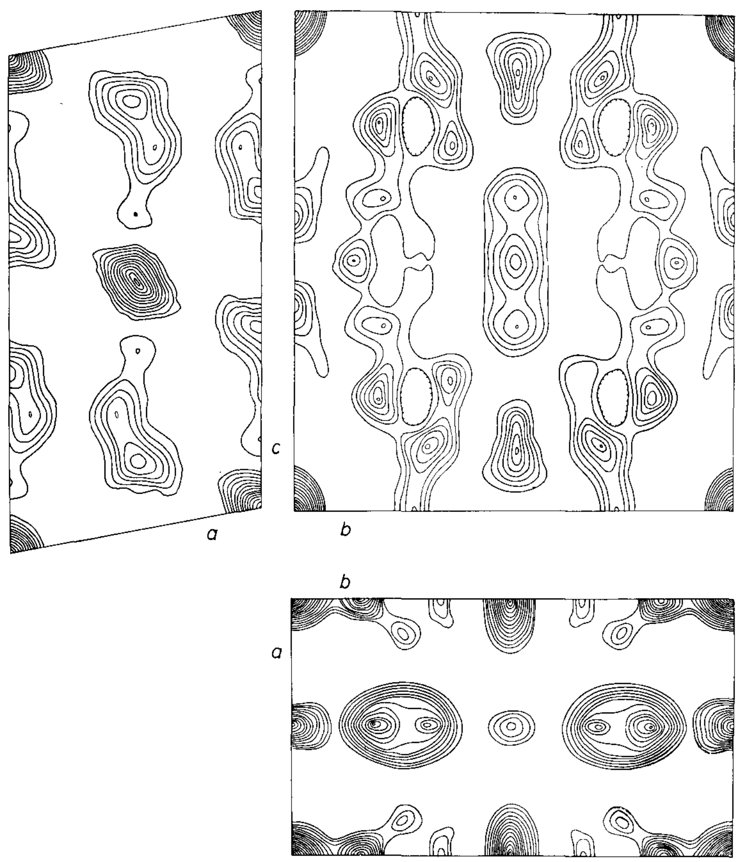


Fig. 1. PATTERSON projections of acanthite on (010), (100) and (001)

[3] M. J. BUERGER and G. KLEIN, Correction of X-ray diffraction intensities for LORENTZ and polarization factors. J. Appl. Physics **16** (1945) 406–418.

The silver atoms were located from PATTERSON projections on the three cell faces (Fig. 1) with the aid of a 0.483, 0.133 $M(xz)$ BUERGER minimum map[4] (Fig. 2) and HARKER-PATTERSON sections $P(xy0)$ and $P(xy\frac{1}{2})$.

From the parameters of the silver atoms the signs of over 80% of the reflections could be determined. Using only these reflections, electron-density projections were plotted on the (001), (010), and (100) faces. From these projections the silver positions could be confirmed but the sulfur positions could not be distinguished from the false detail about the silver peaks.

To distinguish between the sulfur peaks and the false detail a second set of electron-density projections was constructed on the same planes using the same terms as used for the above projections except that the F values were calculated from THOMAS-FERMI scattering factors of the silver positions alone. The sulfur peaks could be identified as those peaks present on the original projections but not present on the second set.

All positions were further refined by successive electron-density maps using all observed terms, and finally by least-squares refinement using the I.B.M. 704 computer as set up by the Service Bureau Corporation of New York. The final electrondensity projections on the three cell faces are shown in Fig. 3. All atoms are located on the fourfold general positions x, y, z; $-x, -y, -z$; $x+\frac{1}{2}, \frac{1}{2}-y, z+\frac{1}{2}$; and $\frac{1}{2}-x, y+\frac{1}{2}, \frac{1}{2}-z$. The final parameters are listed in Table 1. In Table 2 the intensities for all spots of non-zero intensity, as calculated from these parameters, are

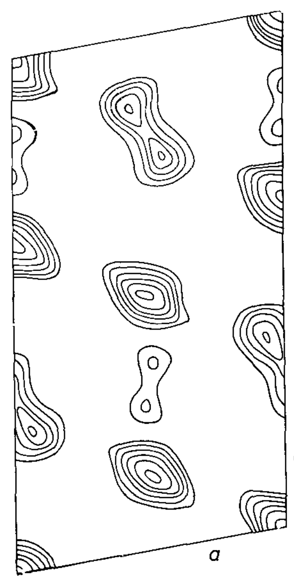


Fig. 2. 0.483, 0.113 $M(xz)$ BUERGER minimum map of acanthite

Table 1. *Parameters of acanthite*

	x	y	z
Ag_I	0.758	0.015	0.305
Ag_{II}	0.285	0.320	0.435
S	0.359	0.239	0.134

[4] M. J. BUERGER, A new approach to crystal-structure analysis. Acta Crystallogr. 4 (1951) 531—544.

compared with those observed. The standard discrepancy factor R is 0.27, and the final isotropic temperature factors are $B_{\mathrm{Ag_I}} = 1.01$; $B_{\mathrm{Ag_{II}}} = 1.16$; $B_{\mathrm{S}} = 0.93$.

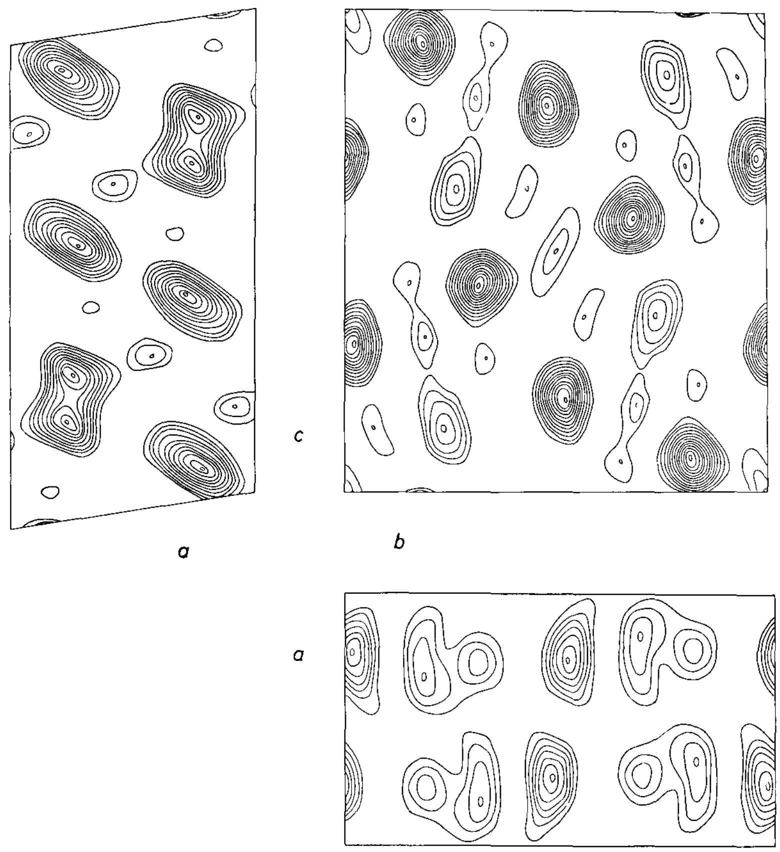


Fig. 3. Electron-density projections of acanthite on (010), (100) and (001)

The structure

The structure of acanthite is illustrated in Fig. 4a and 4b. The sulfur atoms are arranged in a slightly distorted body-centered cubic array with one of the twofold axes of the cube parallel to [010], the 2_1 axis of the monoclinic space group. The faces of the cube lie in the $(10\bar{3})$, (121), and $(\bar{1}21)$ planes. The average length of the cell edge of this sulfur cube is 4.86 Å. There is an almost planar distribution of the sulfur atoms perpendicular to the b axis. One of the Ag atoms lies either a little above or a little below the plane, and is triangularly coordinated to three sulfurs at 2.50 Å, 2.61 Å and 2.69 Å respectively. The other Ag atom lies half way between the planes, and links them together by having one close sulfur in the plane above and one in the plane below at 2.49 Å and 2.52 Å. Table 3 presents a list of the interatomic distances.

Table 2. *Calculated and observed intensities for non-zero reflections*

Index	sinθ	F_{calc}	$\|F\|_{obs}$	Index	sinθ	F_{calc}	$\|F\|_{obs}$	Index	sinθ	F_{calc}	$\|F\|_{obs}$	Index	sinθ	F_{calc}	$\|F\|_{obs}$
040	.446	+119	194	$11\bar{1}$	.224	+ 62	73	$15\bar{6}$	.815	+ 84	53	$21\bar{5}$	.579	+167	37
060	.670	+121	172	$12\bar{1}$	.296	−195	174	117	.758	− 64	79	$22\bar{5}$	.611	+ 54	40
080	.893	+ 5	57	$14\bar{1}$	.486	−106	172	127	.782	+ 73	68	$24\bar{5}$	.722	− 50	46
011	.149	+ 12	33	$15\bar{1}$	.590	− 83	121	137	.821	+ 40	29	$25\bar{5}$	.796	+134	90
031	.334	−168	158	$16\bar{1}$	.696	− 28	66	147	.872	+ 41	18	206	.753	− 24	15
041	.457	− 79	108	$17\bar{1}$	.803	+ 60	86	$10\bar{7}$	690	− 96	53	$20\bar{6}$	.648	+ 96	95
051	.567	+ 48	53	112	.314	−114	132	$11\bar{7}$	.699	− 98	84	$22\bar{6}$	.685	−137	106
061	.677	− 36	79	122	.368	+ 60	73	$13\bar{7}$	.767	+ 52	33	$23\bar{7}$	.805	−154	95
071	.787	− 29	46	132	.445	− 7	20	$14\bar{7}$	.822	− 76	51	$20\bar{8}$	.820	+151	92
002	.199	− 21	26	142	.533	−106	79	128	.875	− 52	37				
012	.228	+ 65	77	152	.629	− 93	90	$12\bar{8}$	818	− 79	66	310	.566	− 29	37
022	.299	−166	128	162	.730	+ 4	22					320	.598	− 59	46
032	.389	+ 36	55	172	.833	− 26	35	200	.370	−215	224	340	.711	+ 26	33
042	.488	− 98	119	$11\bar{2}$	.272	+156	143	210	.386	+ 73	88	360	.868	− 50	33
052	.592	− 39	51	$12\bar{2}$	.333	+ 31	35	220	.432	− 37	33	301	.580	− 75	79
062	.698	− 3	31	$13\bar{2}$	.416	− 39	44	240	.579	− 69	92	311	.590	− 76	88
072	.806	+ 96	134	$14\bar{2}$	.510	− 84	112	250	.668	+ 5	53	321	.621	− 53	40
013	.318	+140	125	$15\bar{2}$	.610	+123	187	260	.764	−105	139	331	.669	+ 41	44
023	.373	+106	95	$16\bar{2}$	.713	− 22	64	211	.414	+ 2	15	341	.731	− 43	48
033	.448	+ 66	68	103	.376	−143	191	221	.457	+ 21	20	351	.804	+ 27	37
043	.537	− 70	70	113	.392	+ 92	139	231	.520	+115	66	361	.885	− 49	48
053	.633	+ 85	97	123	.437	+ 5	29	261	.778	+ 39	44	$31\bar{1}$	.558	− 25	22
063	.733	+ 51	95	153	.672	+ 30	53	$21\bar{1}$	.383	− 6	9	$32\bar{1}$	.591	+ 99	97
073	.836	+ 52	84	163	.767	− 77	103	$22\bar{1}$	.429	+ 45	62	$34\bar{1}$	.706	+ 94	130
004	.398	− 21	42	173	.866	+ 48	44	$23\bar{1}$	.496	+ 93	112	312	.630	+ 51	64
014	.413	+109	117	$10\bar{3}$	.324	+290	224	$24\bar{1}$	.577	−102	136	322	.658	− 39	35
024	.456	+ 60	70	$11\bar{3}$	.343	+ 41	48	$27\bar{1}$	.861	+ 21	44	332	.704	+ 35	20
034	.520	− 63	57	$12\bar{3}$	.393	− 51	81	202	.448	+ 9	11	342	.763	+ 67	24
054	.685	− 82	81	$13\bar{3}$	.465	+ 17	24	212	.462	− 33	53	$31\bar{2}$	.570	− 82	84
064	.779	+ 26	46	$14\bar{3}$	.551	+ 64	84	222	.500	+ 83	64	$32\bar{2}$	.600	+ 12	22
015	.510	−132	108	$15\bar{3}$	.644	+ 37	57	232	.559	− 11	22	$33\bar{2}$	.650	+ 34	35
025	.545	+ 78	77	$16\bar{3}$	.743	+ 85	90	242	.632	+ 82	66	$35\bar{2}$	.788	− 80	90
035	.600	− 46	26	$17\bar{3}$	.844	+ 40	57	272	.899	− 43	44	$36\bar{2}$	870	+ 32	57
045	.668	− 75	46	114	.479	+ 60	70	$20\bar{2}$	.390	+ 33	33	$30\bar{3}$	.585	−162	161
055	.747	−101	81	134	.573	+158	134	$21\bar{2}$	.405	+102	121	$31\bar{3}$	.595	+ 44	68
065	.834	+ 41	68	144	.645	− 11	29	$22\bar{2}$	.449	+149	136	$32\bar{3}$	.626	+ 9	18
006	.597	− 18	35	154	.726	+ 14	29	$24\bar{2}$	.592	+ 53	57	$33\bar{3}$	.673	− 47	48
016	.607	+ 88	92	$11\bar{4}$	.425	− 79	59	$25\bar{2}$	.680	− 32	53	$34\bar{3}$	.735	− 41	37
026	.637	+ 79	64	$12\bar{4}$	.467	− 19	26	$26\bar{2}$	.774	+ 51	75	$36\bar{3}$	.888	− 75	59
046	.745	+ 55	37	$13\bar{4}$	.529	−223	205	$27\bar{2}$	.872	+ 86	64	314	.743	− 34	13
037	.773	+114	88	$14\bar{4}$	.605	+ 31	22	213	.524	− 94	114	$31\bar{4}$	.637	+ 60	20
008	.796	−123	75	$17\bar{4}$	.881	− 59	48	243	.679	+ 38	33	$32\bar{4}$	.665	+ 42	46
				105	.559	− 73	97	253	.757	− 78	57	$33\bar{4}$	.710	+145	114
110	.211	+ 19	20	115	.570	− 32	35	$21\bar{3}$	.449	− 99	86	$34\bar{4}$	.769	− 63	77
120	.289	+125	106	165	.871	− 72	77	$22\bar{3}$	.489	+101	97	305	.804	+ 54	35
130	.382	− 15	22	$10\bar{5}$	.501	+100	99	$23\bar{3}$	.549	− 93	84	$30\bar{5}$	.681	− 67	62
140	.482	− 54	59	$11\bar{5}$	.513	− 53	51	$24\bar{3}$	.623	− 64	57	$31\bar{5}$	.690	+ 74	68
160	.693	+ 72	99	$12\bar{5}$	.548	− 32	42	$25\bar{3}$	.707	− 58	77	$32\bar{5}$	.717	+ 46	55
180	.910	+ 69	64	$13\bar{5}$	.602	− 43	51	$27\bar{3}$	.893	− 38	22	$31\bar{6}$	.753	− 93	51
101	.224	+ 62	95	$15\bar{5}$	.749	+ 15	42	204	.587	− 32	33	$32\bar{6}$	.777	+ 61	62
111	.250	+114	108	$16\bar{5}$	.835	+ 63	70	214	.597	− 71	40	$33\bar{6}$	.816	− 77	35
121	.316	+167	123	116	.663	− 87	73	224	.627	+ 10	13	$34\bar{6}$	.868	− 81	59
131	.402	− 39	51	146	.791	+ 54	46	234	.675	+ 51	35	$30\bar{7}$	.815	+118	75
141	.499	+ 62	92	156	.859	− 76	29	$20\bar{4}$	.496	+ 43	55	$31\bar{7}$	.823	+ 50	35
151	.600	− 67	121	$11\bar{6}$	.605	+123	75	$21\bar{4}$	.509	+ 55	57	$33\bar{7}$	.881	− 18	59
161	.705	+ 68	136	$12\bar{6}$	.635	− 64	64	$22\bar{4}$	.544	− 84	75	$31\bar{8}$	.899	+ 74	48
181	.919	+ 34	37	$14\bar{6}$	.743	+ 89	88	$25\bar{4}$	.746	−103	110				

Polymorphism and twinning

When Ag_2S crystallizes above 173° argentite crystals with cubic symmetry and morphology are formed. Upon cooling, a single crystal of argentite rapidly inverts to a polycrystalline body of acanthite while retaining the cubic morphology. After the transformation one twofold axis of the cube is retained as the twofold screw or b axis of the monoclinice acanthite. As there are six twofold axes to a cube there are also six possible orientations the acanthite can take with respect to the argentite morphology. The usual case is to have several, if not all, of these orientations as small intergrowing domains.

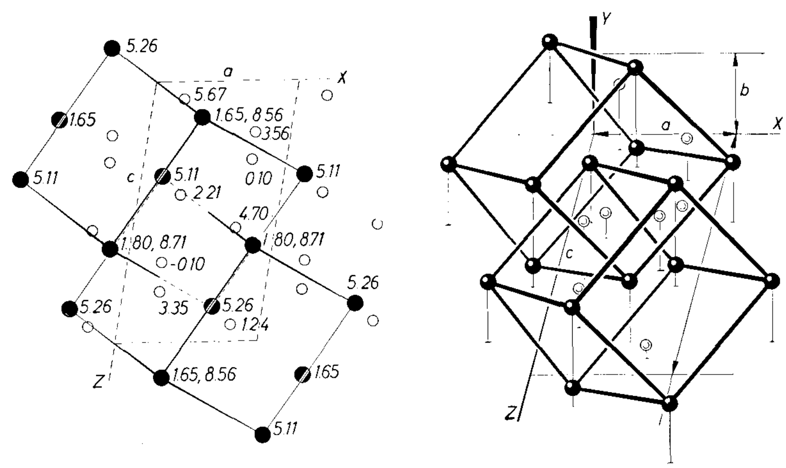


Fig. 4. The structure of acanthite, dark circles represent sulfur atoms, light circles silver atoms. (a) Orthogonal projection perpendicular to the b axis; (b) Projection inclined 20° to b axis. y co-ordinates in Å

Table 3. *Some interatomic distances in acanthite*

Atom	Neighbor	Distance
Ag_I	Ag_I	3.41; 3.56; 3.57
	Ag_{II}	3.04; 3.12; 3.14; 3.19
	S	2.49; 2.52; 3.07
Ag_{II}	Ag_{II}	3.15; 3.73
	S	2.50; 2.61; 2.69
S	S	4.08; 4.09; 4.15; 4.19

Fig. 5 will serve to illustrate the domain structure of a small cube of "argentite" from Freiberg, Saxony (Harvard University Museum No. 93079). Fig. 5a shows the zero-level, a axis BUERGER precession photograph of argentite taken above 200°C. Fig. 5 b is a picture taken at the same setting of the same crystal at room temperature. Fig. 5c is a zero-level, $[10\bar{3}]^*$ direction, precession picture of a single crystal of acanthite. It can be seen that if Fig. 5c were rotated 90° about the precession axis, $[10\bar{3}]^*$, and superimposed upon itself it would produce Fig. 5b. The pictures taken by precessing about the other morphological cube axes are identical to that of Fig. 5b.

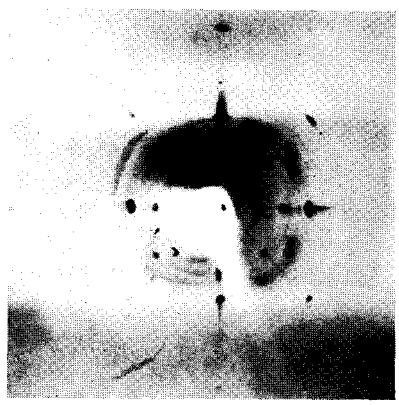
Attempts to find a statistical arrangement of the silver atoms for the high-temperature form based upon the silver positions in the low form did not yield calculated intensities as close to the observed intensities as those determined by RAHLFS for the parameters mentioned in the introduction of this paper.

Fig. 5. BUERGER precession photographs of Ag_2S (Mo $K\alpha$).

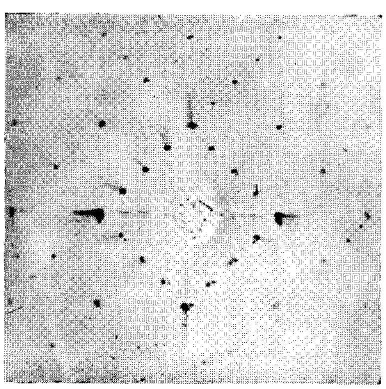
(a) Zero level a axis of argentite above 200° C.

(b) Same setting as (a) at room temperature.

(c) Zero level [103]* of acanthite



5a



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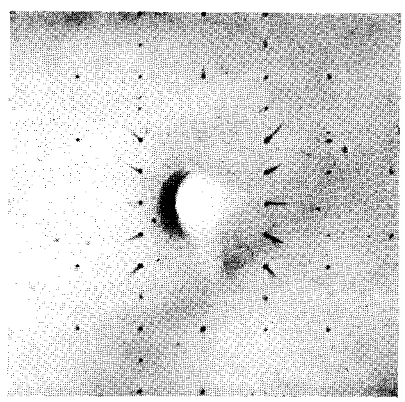

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Acknowledgements

This work is part of a research program on the crystal chemistry of the sulfides, made possible, in part, by a grant from the National Science Foundation. The author wishes to express his appreciation to Prof. CLIFFORD FRONDEL, Prof. LEWIS RAMSDELL, Dr. GEORGE SWITZER and ALBERT FORSLEV for supplying the crystals investigated. The technical assistance of Mr. DAVID NORTHROP is gratefully acknowledged.

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