THE STRUCTURE OF MIARGYRITE

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Introduction. The structure of miargyrite ($AgSbS_2$) has been determined in part by Hofmann (1938) and more completely by Knowles (1964). Hofman located the heavy atoms from the strong reflections, but made no intensity measurements. Knowles made a complete determination with a single-crystal diffractometer. His results were considerably different, giving the space group Cc rather than the more centrosymmetric C2/c of Hofman. Least-squares analysis gave an R value of 0.27 for the Cc group but only 0.13 for C2/c. Since all other possibilities have been eliminated by the systematic extinctions, C2/c was taken as the space group. The following investigation was carried out to verify this structure.

Experimental. The sample was supplied by Prof. Barclay Kamb and is from the Kelly Mine at Randsburg, California. Because of high absorption an attempt was made to grind a sphere of the material, but anisotropic hardness resulted in prolate ellipsoids elongated along the b axis. The one I used measured 0.16x0.17x0.22 mm, and an absorption correction was applied for a sphere of diameter 0.017 cm. μ was calculated as 1187 cm^{-1} from the International Tables of X-ray Crystallography, and the structure factors were calculated with the CRYRM computer program written by David Duchamp.

The intensities were measured by the multiple-film Weissenberg technique, using both unfiltered Cu and Cu Kα radiation. The two crystals I examined showed some damage from grinding; the reflections with small θ

Table 1. Observed Structure Amplitudes

h	0	l	sin θ	This work	Knowles
2	0	0	0.121	< 21	82
4	0	0	.242	248	212
6	0	0	.364	<10	9
8	0	0	.485	173	291
10	0	0	.606	14	22
12	0	0	.727	53	137
14	0	0	.849	<3	9
0	0	2	.118	46	25
2	0	2	.181	74	50
4	0	2	.285	<13	9
6	0	2	.399	< 9	16
8	0	2	.516	44	91
10	0	2	.635	326	74
12	0	2	.754	9	20
14	0	2	.874	9	11[illegible]
0	0	4	.236	48	30
2	0	4	.281	431	385
4	0	4	.363	28	20
6	0	4	.462	145	199
8	0	4	.570	13	19
10	0	4	.683	75	175
12	0	4	.798	6	16
14	0	4	.914	25	103
0	0	6	.354	24	22
2	0	6	.391	75	67
4	0	6	.458	58	60
6	0	6	.544	< 7	2
8	0	6	.642	7	14
10	0	6	.746	32	83
12	0	6	.855	16	58
0	0	8	.472	141	181
2	0	8	.504	33	40
4	0	8	.562	137	220
6	0	8	.638	2	30
8	0	8	.726	66	147
10	0	8	.822	8	20
12	0	8	.925	21	88
0	0	10	.590	18	29
2	0	10	.620	12	14
4	0	10	.671	43	74
6	0	10	.738	25	47
8	0	10	.818	6	8
10	0	10	.907	16	3
0	0	12	.708	15	36
2	0	12	.736	59	135
4	0	12	0.782	14	33
6	0	12	.843	40	123
8	0	12	.916	10	38
0	0	14	.826	9	27
2	0	14	.852	5	16
4	0	14	.895	9	3
6	0	14	.951	13	65
0	0	16	.944	22	108
2	0	16	.969	8	45
-2	0	2	.156	<[illegible]	10
-4	0	2	.249	[illegible]8	6
-6	0	2	.356	5[illegible]	57
-8	0	2	.469	43	71
-10	0	2	.584	2	17
-12	0	2	.700	5	8
-14	0	2	.816	20	63
-2	0	4	.253	2[illegible]	205
-4	0	4	.312	<[illegible]	4
-6	0	4	.403	297	326
-8	0	4	.506	22	34
-10	0	4	.617	64	144
-12	0	4	.730	<5	6
-14	0	4	.846	46	148
-2	0	6	.356	30	32
-4	0	6	.398	<9	3
-6	0	6	.468	21	25
-8	0	6	.556	14	17
-10	0	6	.654	8	13
-12	0	6	.760	17	47
-14	0	6	.869	17	60
-2	0	8	.469	16	23
-4	0	8	.497	161	279
-6	0	8	.550	29	57
-8	0	8	.624	57	140
-10	0	8	.710	< 5	7
-12	0	8	.805	40	174
-14	0	8	.907	7	34
-2	0	10	.584	26	27
-4	0	10	.603	11	28
-6	0	10	.645	6	18
-8	0	10	.705	12	35
-10	0	10	.780	6	16
-12	0	10	.865	9	43
-2	0	12	.700	576	194
-4	0	12	.713	16	52
-6	0	12	.746	29	121

h	0	l	sin θ	This work	Knowles
-8	0	12	0.796	< 4	16
-10	0	12	.860	27	163
-12	0	12	.936	12	52
-2	0	14	.816	10	48
-4	0	14	.825	9	13
-6	0	14	.851	8	41
-8	0	14	.893	7	3

Table 2. Atomic Co-ordinates

Atom		Knowles	Postulated C2/c Structure	
Ag(1)	x:	0.0000	0	0
Ag(2)		0.0091±0.0004	0	0
Sb(1)		0.2585±0.0002	x	0.2585
Sb(2)		0.7486±0.0004	1-x	0.7415
S(1)		0.1457±0.0008	x'	0.1457
S(2)		0.8612±0.0009	1-x'	0.8543
S(3)		0.1161±0.0008	x"	0.1161
S(4)		0.8966±0.0010	1-x"	0.8839
Ag(1)	y:	0.0000	0	0
Ag(2)		0.5173±0.0023	$\frac{1}{2}$	0.5000
Sb(1)		0.9568±0.0016	0	0
Sb(2)		0.0526±0.0017	0	0
S(1)		0.3754±0.0046	y	0.3754
S(2)		0.6709±0.0052	1-y	0.6246
S(3)		0.1815±0.0046	y'	0.1815
S(4)		0.8399±0.0035	1-y'	0.8185
Ag(1)	z:	0.2500	$\frac{1}{4}$	0.2500
Ag(2)		0.4996±0.0004	$\frac{1}{2}$	$\frac{1}{2}$
Sb(1)		0.6207±0.0002	z	0.6207
Sb(2)		0.3652±0.0004	1-z	0.3793
S(1)		0.6875±0.0010	z'	0.6875
S(2)		0.2941±0.0011	1-z'	0.3125
S(3)		0.4072±0.0008	z"	0.4072
S(4)		0.5757±0.0010	1-z"	0.5928

were especially diffuse, so many of them are suspect. Although Knowles used a diffractometer, his data may be subject to some of the same error. An additional error in this work is the fact that the spots vary considerably in shape. Structure factors for the zero-layer line, as measured in this work, are compared with Knowles' in Table 1. Measurement of the others is in progress.

Discussion. Packing considerations suggest a structure similar to that of galena, but the S atoms, as determined by Knowles, vary considerably from the postulated positions. Furthermore, there are two non-equivalent sets of Ag atoms and of Sb atoms. The Sb atoms have trigonal co-ordination, while the Ag atoms have tetrahedral and two-fold co-ordination. The additional symmetry found in the C2/c space group would require that similar metal atoms be equivalent and would reduce the number of non-equivalent S atoms to two. Thus a slight shift, such as that shown in Table 2, would result in more "normal" three-fold co-ordination for Ag. It is for this reason that this project is being done.

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