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THE CRYSTAL STRUCTURE OF THE LOW-TEMPERATURE FORM OF SILVER SELENIDE

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ABSTRACT

The crystal structure of the low-temperature form of Ag_2Se (Ag_2Se II, naumannite, stable below 133°C) has been determined by X-ray powder methods. The structure differs from the one found by Pinsker *et al.* by electron diffraction studies of thin sublimed layers.

Ag_2Se is orthorhombic with unit-cell dimensions a 4.333, b 7.062, c 7.764 Å. The space group is $P\,2_12_12_1$ and there are four units Ag_2Se in the unit cell. All atoms lie on the fourfold general positions. The structure is closely related to the structure of the monoclinic modification of silver sulfide (Ag_2S III, acanthite). There is an almost planar distribution of selenium atoms perpendicular to the b axis. There are two types of structurally different silver atoms. Silver atoms of type I lie close to the planes of selenium atoms and are coordinated almost tetrahedrally by selenium at distances of 2.62, 2.76, 2.79, and 2.86 Å. Silver atoms of type II lie halfway between the planes of selenium; they are coordinated triangularly by selenium at distances of 2.72, 2.76, and 2.81 Å.

The anion packing is essentially body-centered cubic.

INTRODUCTION

Silver selenide, Ag_2Se, occurs at atmospheric pressure in two polymorphic forms. The high-temperature form, form I, is stable above 133°C. The structure is body-centered cubic with spacing $a = 4.983$ Å; the unit cell contains two units Ag_2Se. The selenium atoms form a body-centered packing, while the silver atoms are statistically distributed over several types of interstitial sites (Rahlfs, 1936).

The low-temperature form, Ag_2Se II, stable below 133°C, is known as the mineral naumannite. Ag_2Se is orthorhombic with cell constants a 4.344, b 7.111, and c 7.790 Å (Conn and Taylor, 1960). There are four units Ag_2Se in the unit cell. The structure of thin sublimed films has been determined by Pinsker *et al.* (1965) by electron diffraction investigation. The cell constants, a 4.325, b 7.05, and c 7.82 Å agree with those reported by Conn and Taylor. The space group is given as $P\,2_122$. The silver atoms form a framework of a diamond-type lattice; the Ag-Ag distances are short, ranging from 2.61 to 2.82 Å (in metallic silver 2.89 Å). This structure is penetrated by Ag-Se-Ag-Se chains with Ag-Se distances of 2.54 Å.

The intensities of the X-ray powder lines of Ag_2Se II observed by Early (1950), Novoseleva *et al.* (1967) and by us are, however, in disagreement with the intensities calculated from the atomic parameters given by Pinsker *et al.*

By comparing the cell constants (Table 1) and intensities of the powder lines of Ag_2S III (U.S. Nat. Bur. Stan., 1960) and Ag_2Se II a resemblance is noted, which suggests a close relationship of both structures. The structure of Ag_2S III has been determined by Frueh (1958) by single-crystal methods. The space group is $P\ 2_1/n$ and there are four units Ag_2S in the unit cell. All atoms are located on fourfold general positions (Table 1). There is an almost planar distribution of sulfur atoms perpendicular to the *b* axis. There are two types of silver atoms; silver atoms of type I lie slightly above or below the planes of sulfur and are triangularly coordinated to sulfur atoms at distances of 2.50, 2.61, and 2.69 Å.

Silver atoms of type II lie halfway between the planes of sulfur and link them together by having one close sulfur atom in the plane above and one in the plane below; the Ag-S distances are 2.49 and 2.52 Å respectively. 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.

TABLE 1. CRYSTAL DATA OF Ag_2S III AND Ag_2Se II

		Ag_2S III			Ag_2Se II		
cell constants		a = 4.229 Å			a = 4.333 Å		
		b = 6.931 Å			b = 7.062 Å		
		c = 7.862 Å			c = 7.764 Å		
		β = 99.61					
space group		$P\ 2_1/n$			$P\ 2_12_12_1$		
coordinates of equivalent positions		x,y,z; $\bar{x},\bar{y},\bar{z}$ 1/2+x,1/2-y,1/2+z; 1/2-x,1/2+y,1/2-z			x,y,z; 1/2+x,$\bar{y},\bar{z}$; $\bar{x}$,1/2-y,1/2+z; 1/2-x,1/2+y,1/2-z.		
		x	y	z	x	y	z
coordinates	Ag I	.285	.320	.435	.107(4)	.369(2)	.456(2)
	Ag II	.758	.015	.305	.728(4)	.029(2)	.361(2)
	S or Se	.359	.239	.134	.358(4)	.235(3)	.149(4)

The cell constants of Ag_2S III are the more accurate ones determined by the N.B.S. (1960) The origin in the cell of Ag_2Se II is shifted over $\frac{1}{4}\frac{1}{4}0$ compared with the origin in the conventional setting (International Tables for Crystallography, I; see text). Standard deviations, in units of the last decimal place, are given in parentheses.

The structure of Ag_2Se II could easily be solved by X-ray powder methods taking into account the relationship of the diffraction patterns of Ag_2Se II and Ag_2S III. No attempts were made to investigate single crystals. In the case of Ag_2S a single crystal of the body-centered cubic form (form II, stable between 176 and 600°C) on cooling rapidly converts to a polycrystalline species of the monoclinic form while retaining the cubic morphology (Frueh, 1958; Taylor, 1969). The same conversion probably occurs in Ag_2Se.

EXPERIMENTAL

Ag_2Se was prepared from the elements in the stoichiometric proportion. The mixture of the elements was heated at 500°C for four days in an evacuated quartz tube, followed by slow cooling (10°C per hour) to room temperature.

X-ray powder patterns were registered by a Philips diffractometer and a Guinier-de Wolff camera (Nonius); CuKα radiation was used in both cases. The powder pattern essentially agreed with that of the mineral naumannite (Early, 1950; good agreement was found with the powder pattern of synthetic Ag_2Se published by Novoseleva *et al.* (1967).

Accurate d-values were obtained from a Guinier photograph; silicon powder ($a = 5.4305$ Å) was used as an internal standard. The cell constants obtained by least-squares are $a = 4.333$, $b = 7.062$, and $c = 7.764$ Å; the standard deviation is 0.05 percent.

The intensities of the powder lines were measured by planimetering of the diffractograms.

Atomic positions were refined by means of the least-squares program T53C written by Dr. H. M. Rietveld (R.C.N., Petten, The Netherlands). This full-matrix program permits to include overlapping powder lines in the calculations.

DETERMINATION OF THE STRUCTURE

The systematic extinctions: $h00$, $0k0$, and $00l$ reflections only present for $h, k, l = 2n$, are in agreement with space group $P\,2_12_12_1$. In the monoclinic cell of Ag_2S III, space group $P\,2_1/n$, the atoms occupy the fourfold general positions: x,y,z; $\bar{x},\bar{y},\bar{z}$; $\frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}+z$; $\frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}-z$. The coordinates of the three independent atoms are given in Table 1. The fourfold general positions in space group $P\,2_12_12_1$ are x,y,z; $\frac{1}{2}+x,\bar{y},\bar{z}$; $\bar{x},\frac{1}{2}-y,\frac{1}{2}+z$; $\frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}-z$ if the origin is shifted over $\frac{1}{4}\frac{1}{4}0$ compared with the origin in the conventional setting halfway between the three non-intersecting twofold screw axes (International Tables for Crystallography, I), in order to demonstrate the relationship with the fourfold positions in space group $P\,2_1/n$. The (100) projections in both space groups have the same symmetry.

The intensities of the $0kl$ reflections of Ag_2Se II were calculated using the coordinates of the corresponding atoms in Ag_2S III. The agreement between calculated and observed intensities was reasonable and a refinement was carried out with 15 $0kl$ reflections. The index $R_I = 100\sum|I_0 - I_c|/I_0$ was 14 percent. Starting values for the x coordinates were found by trial and error. A least-squares refinement was carried out with 64 *hkl* reflections including 13 non-observed reflections, covering all possible reflections down to $d=1.41$ Å. The atomic scattering factors were those given by Moore (1963). All atoms were assumed to have the same (isotropic) temperature factor. Nine positional parameters, one scaling factor, and one temperature factor were also refined. The final agreement is good, the index R_I being 8.3 percent. The coefficient B in the temperature factor was 0.75 Å^2. The coordinates and the standard deviations are given in Table 1. Observed and calculated intensities are compared in Table 2.

DISCUSSION OF THE STRUCTURE

The distances between the atoms were calculated using the coordinates given in Table 1. The standard deviations in the distances are about 0.03 Å. The (100) projections of Ag_2S III and Ag_2Se II are shown in Figure 1.

In both structures there is an almost planar arrangement of chalcogen atoms perpendicular to the *b* axis. There are two types of structurally different silver atoms. Silver atoms of type I lie a little above or below (in Ag_2S 0.49 Å, in Ag_2Se 0.84 Å) the planes of the chalcogen atoms. In Ag_2S silver atoms of type I have a distorted tetrahedral coordination by sulfur. Three sulfur atoms are lying in the nearest plane, the Ag-S distances being 2.50, 2.61, 2.69 Å; the fourth sulfur atom lies in the next plane, the Ag-S distance is 3.00 Å. In Ag_2Se the silver atoms of type I are tetrahedrally coordinated, the Ag-Se distances are 2.62, 2.79, 2.86 Å (to selenium atoms lying in one plane), and 2.71 Å (to selenium in the next plane).

The silver atoms of type II lie about halfway between the planes of chalcogen atoms. In Ag_2S these silver atoms have five sulfur neighbours at distances of 2.49, 2.52, 3.07, 3.33, and 3.44 Å. The coordination by sulfur at the short distances of 2.49 and 2.52 Å is almost linear. In Ag_2Se the Ag-Se distances of silver of type II are 2.72, 2.74, 2.81, 3.28, and 3.50 Å. The coordination of silver by selenium at the distances of 2.72, 2.74, and 2.81 Å is almost triangular.

It may be noted that Ag_2Te III also has two structurally different types of silver. Silver atoms of type I are surrounded by four tellurium atoms at distances of 2.87, 2.91, 3.04, and 2.99 Å forming a somewhat distorted tetrahedron. The other silver atoms have each five close tellurium atoms at distances of 2.85, 2.90, 2.95, 3.01, and 3.04 Å (Frueh, 1959).

The complicated stereochemistry of silver in chalcogenides has been ascribed to *d-s* mixing (Orgel, 1958). It may be seen from Table 3 that

Table 2. Observed and calculated intensities of Ag_2Se II.

hkl	d_{calc}	I_c	I_o	hkl	d_{calc}	I_c	I_o	hkl	d_{calc}	I_c	I_o
011	5.224	3	<3	032	2.013	143	150	141	1.600	7	<5
002	3.882	48	37	211	2.001	84	90	230	1.594	42	36
101	3.784	8	10	131	1.999	19		124	1.583	3	<5
110	3.693	4	8	004	1.941	33	40	231	1.562	43	36
020	3.531	4	6	202	1.892	8	<4	015	1.517	5	<5
012	3.402	4	<3	123	1.881	81	136	142	1.507	4	<5
111	3.335	48	42	014	1.872	51		223	1.503	11	12
021	3.214	3	<3	220	1.847	29	25	034	1.498	0	<5
102	2.891	97	98	212	1.827	33	62	232	1.475	27	22
120	2.737	129	123	132	1.825	26		105	1.462	22	17
112	2.676	608	600	221	1.797	19	21	043	1.458	3	
022	2.612	0	<3	104	1.771	11	15	204	1.446	26	14
121	2.581	536	509	040	1.766	3		115	1.431	6	<5
013	2.430	185	187	033	1.741	6	<5	025	1.421	40	53
031	2.253	192	200	041	1.722	5	36	301	1.420	26	
122	2.237	107	100	114	1.718	31		214	1.416	10	30
103	2.222	2	<3	024	1.701	5	<5	134	1.415	15	
200	2.167	33	20	222	1.668	7	12	310	1.415	3	
113	2.119	183	208	203	1.661	2	<5				
023	2.087	19	210	140	1.635	19	8				
201	2.087	171		213	1.617	37	55				
210	2.071	15	75	133	1.616	14					
130	2.068	50		042	1.607	41	31				

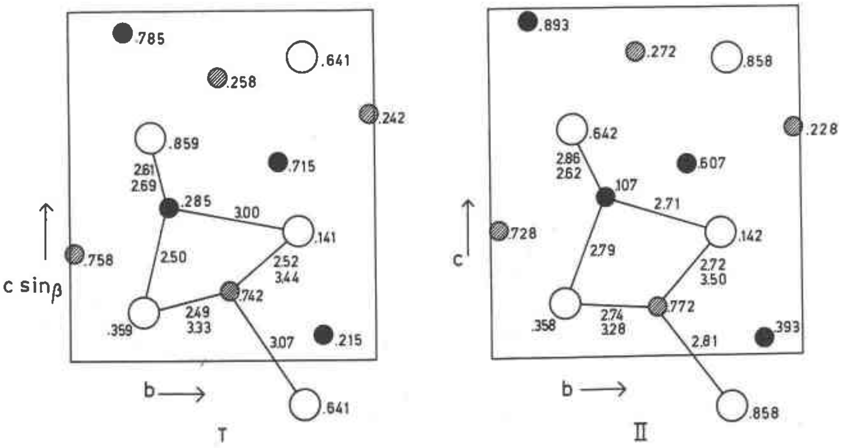

FIG. 1. (100) projections of (I) Ag_2S III and (II) Ag_2Se II. Sulfur and selenium atoms are shown as large open circles; silver atoms of type I as black circles and silver atoms of type II as hatched circles. The distances are in Å; x coordinates of the atoms are also given.

the number of coordinating atoms in compounds Ag_2X increases in the series X = O, S, Se, Te as may be expected from the size of the anions.

In both compounds Ag_2S III and Ag_2Se II each chalcogen atom is surrounded by nine silver atoms, six silver atoms forming a trigonal prism, the remaining three silver atoms are approximately in one plane with chalcogen.

There are no short Ag-Ag distances in the two compounds; the dis-

TABLE 3. COORDINATION OF SILVER BY CHALCOGEN IN COMPOUNDS Ag_2X

	Ag (I)-X	Ag(II)-X
Ag_2O	2.044, 2.044 Å linear	-
Ag_2S III	2.50, 2.61, 2.69 Å (3.00 Å) pyramidal (tetrahedral)	2.49, 2.52 Å (3.07, 3.33, 3.44 Å) linear (square pyramidal)
Ag_2Se II	2.62, 2.71, 2.79, 2.86 Å tetrahedral	2.72, 2.74, 2.81 Å (3.28, 3.50 Å) triangular (square pyramidal)
Ag_2Te III	2.85, 2.90, 2.95, 3.01, 3.04 Å trigonal bipyramidal	2.87, 2.91, 2.99, 3.04 Å tetrahedral

References: Ag_2O: Wyckoff, (1963); Ag_2S III: Frueh, 1958; Ag_2Se II: this work; Ag_2Te: Frueh, 1959.

The coordination is only approximate (except for Ag_2O). In parenthesis are given chalcogen atoms at somewhat larger distances and the coordination if these chalcogen atoms are also taken into account.

tances range from 3.04 to 3.71 Å in Ag_2S III and from 2.93 to 3.68 Å in Ag_2Se II.

The anion packing in both compounds is essentially body-centered cubic, one of the twofold axes of the cube being parallel to [010]. In Ag_2S III the cube is only slightly distorted, in Ag_2Se II the distortion is larger. The (fourteen) Se-Se distances range from 3.98 to 5.14 Å. In the high-temperature body-centered cubic form I the Se-Se distances are 4.30 Å (8x) and 4.98 Å (6x).

The structure of Ag_2Se found by Pinsker *et al.* (1965) by electron diffraction is completely different from the structure described here; it might correspond to a form which is only stable in thin layers.

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