STRUCTURAL AND THERMODYNAMIC PROPERTIES OF SILVER IODIDE

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(1960)

Submitted In Partial Fulfillment

of the Requirements for the

Degree of Master of Science

at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

May 1960

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Department of Geology and Geophysics, 21 May 1960

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Submitted to the Department of Geology and Geophysics, Massachusetts Institute of Technology on 23 May 1960 in partial fulfillment of the requirements for the degree of Master of Science.

ABSTRACT

Silver iodide exists in four different crystalline modifications: a low-temperature cubic form with the sphalerite structure, a hexagonal form with the wurtzite structure, a high-temperature form with a disordered body-centered cubic structure, and a high-pressure sodium-chloride type cubic structure. The published thermodynamic data for silver iodide at normal temperature and pressure differ to the extent of several hundred calories in ΔH_f and ΔF_f because of the failure of previous investigators to distinguish between the low-temperature cubic and hexagonal phases in their thermochemical measurements.

In this investigation both the wurtzite and sphalerite structures of AgI (as identified by x-ray diffraction methods) have been prepared by several independent, reproducible methods. These results confirm the reports of previous investigators that both forms exist, whether stable or metastable, between 25° and 100°C. under one atmosphere pressure. The sphalerite form was prepared by water dilution of a concentrated AgI-$AgNO_3$ solution, and also by digestion of HgI_2 in a dilute aqueous $AgNO_3$ solution. The wurtzite form was prepared by water dilution of a concentrated AgI-KI aqueous solution, by digesting metallic silver in an aqueous triiodide solution, and by digesting solid AgI in hot concentrated NH_4OH. The wurtzite structure was converted to the sphalerite structure by grinding. X-ray diffraction data are presented for AgI (sphalerite structure), AgI (wurtzite structure), and for the double salts $AgI \cdot AgNO_3$ and $AgI \cdot 2AgNO_3$. Several new, but predicted, diffraction lines are reported for the sphalerite structure of AgI.

Heats of solution have been measured for the change in state:

AgI (sphalerite structure) = AgI (wurtzite structure),

ΔH = -110 cal./mole.

These are the only thermodynamic measurements on samples of silver iodide in which the structures are adequately characterized. The observed difference in heat oontent is the same order of magnitude as the discrepancies among the existing standard heats of formation, ΔH_f.

The solid state conversion of the wurtzite form of silver iodide to the sphalerite form is extremely slow, if it takes place at all at normal temperature and pressure. The relative stabilities of the silver iodide wurtzite and sphalerite structures cannot be determined without additional data; however, with the heats of solution measurements and other qualitative evidence, it is concluded that the wurtzite form is stable at 1 atm. from room temperature to 146°C. where it converts to the high temperature cubic form. The sphalerite form, which also converts to the high-temperature cubic near 146°C., is probably not stable at any temperature under one atmosphere pressure.

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II. INTRODUCTION

1. Summary of Previous Work

Silver iodide, unlike silver chloride and silver bromide which possess sodium-chloride type structures, is reported to exist in four crystalline modifications: a low-temperature cubic (ltc) with the sphalerite structure, a hexagonal form (hex) with the wurtzite structure, a high-temperature form (htc) with a disordered cubic structure, and a high-pressure sodium-chloride type cubic (hpc) structure.

Tammann (1911) and Bridgman (1915, p. 97) studied the high-pressure form. Bridgman investigated an uncharacterized AgI reagent from 30 to 200°C. and from 0 to 20,000 kg./cm.^{2} pressure and found three forms of silver iodide: hexagonal, high-temperature cubic, and high-pressure cubic with the triple point at 2810 kg. and 99.4°C. The hexagonal to high-pressure cubic transition at room temperature occurred at 3000 kg. pressure.

A cubic structure of the sphalerite type was reported by Wilsey (1921) and confirmed by Davey (1922). Aminoff (1922a, 1922b) pointed out that the mineral iodyrite was known to have hexagonal symmetry, and confirmed this by Laue diffraction patterns obtained from a cleavage sheet with the x-ray beam normal to (001), the cleavage plane, or to (100). Wilsey (1923) studied the powder photographs from samples of silver iodide precipitated from silver nitrate solution by

potassium iodide, and concluded, from the variation of intensity of diffraction lines common to both proposed structures and from the presence of lines not common to both, that the sphalerite and wurtzite forms occurred together in varying proportions; the only difference being that of cubic and hexagonal close packing of the iodides. This was confirmed by Barth and Lunde (1926) who found that samples of powdered iodyrite were never purely hexagonal but always contained some of the cubic form, and that pure cubic samples could be obtained from silver iodide precipitated from solution and dried at 100°C.

Bloch and Moller (1931) found that the pure low-temperature cubic form was obtained by powdering any coarse crystalline preparation, e.g. that solidified from a melt. The pure hexagonal form was obtained by dissolving any AgI preparation in concentrated KI solution followed by precipitation of the silver iodide by dilution, or by precipitation from HI or $Hg(NO_3)_2$ solution, or by allowing silver iodide to solidify from the melt with no further handling such as powdering or reheating. Samples precipitated from KI and $AgNO_3$ solution always yielded a mixture of the cubic and hexagonal forms from which the diffraction lines (400), (331), and (620), characteristic only of the cubic form, were obtained in addition to the characteristic hexagonal lines. The fraction with the sphalerite structure was increased by using strongly diluted solutions and a large excess of $AgNO_3$. Bloch and Moller

concluded that during precipitation the cubic silver iodide is formed primarily, but at once partly dissolves in excess KI and later is reprecipitated, on washing, as the hexagonal form; so that the cubic form can never be obtained pure by precipitation. Both the cubic (ltc) and hexagonal forms were converted into the same new form (htc) at about 146°C., and the x-ray patterns from different samples at various temperatures above 165°C. were the same, but a determination of the structure was not carried out. The remarkable fact was established that the proportions of the hexagonal and cubic forms in any sample were effectively unchanged by once heating above the 146°C. transition point and then cooling again (e.g. the pure cubic form remained cubic and the pure hexagonal form remained hexagonal), although the patterns obtained above the transition point were all similar. Initially pure hexagonal samples yielded a small fraction of the low-temperature cubic form on cooling after having been heated to near the melting point (550°C.) for several hours, but no hexagonal form was detected in pure cubic samples which had undergone the same treatment. By heating pure cubic and pure hexagonal samples for six weeks ~~and~~ 125°$\pm$5° and 135°$\pm$5°C. it was found that the hexagonal form is the stable one between 146°C. and 135°C., and the cubic form is stable below 135°C. This was also confirmed by the action of iodine on silver mirrors deposited on thin glass rods, although their actual temperature during iodization was rather doubtful. This reaction above 146°C. yielded the

pure low-temperature cubic form of silver iodide, while just below the transition temperature both cubic and hexagonal types were obtained, and the specimens formed below 135°C. were always pure cubic. Finally, Bloch and Moller also found that sublimed silver iodide consisted mostly of cubic and hexagonal mixtures, though one sample was pure hexagonal.

Kolkmeijer and van Hengel (1934), found that silver iodide was precipitated from solution in the cubic (ltc) form in the presence of excess Ag^+ ions, and in the hexagonal form in the presence of excess I^- ions. The hexagonal form was prepared by dissolving silver iodide in KI solution, filtering, diluting, and washing the precipitate until no I^- ions could be detected by their reaction with $AgNO_3$. Strock (1934, 1935) obtained Debye-Scherrer photographs of silver iodide at a temperature between 230 and 250°C. Using a silver pattern for calibration he determined the lattice constant of the high-temperature cubic form, and concluded from the intensities of the diffraction lines that with two molecules per unit cell the iodine atoms must form a body-centered cubic lattice in which two silver atoms have a choice of 42 sites, not all of which have the same coordination number.

Helmholtz (1935) used powder, Laue, and oscillation methods, and concluded that at 93°K. the structure of the hexagonal form is essentially that of wurtzite with the ideal parameter value for regular tetrahedral arrangement,

while at room temperature the silver ions appear to be distributed at random among the four positions tetrahedrally surrounding the ideal position. However, Pitzer (1941) observed that the smoothness of the heat capacity curve eliminates the possibility of separate, distinct potential minima within a tetrahedron. Unfortunately, as in most of the thermodynamic measurements made on silver iodide, Pitzer failed to characterize the structure of sample on which he made his measurements; it was prepared by mixing dilute solutions of KI and $AgNO_3$ and dried at 150°C. for several days, and was, therefore, probably a mixture of the cubic and hexagonal forms. Helmholtz formed relatively large hexagonal crystals by saturating a concentrated HI solution with AgI and spreading a thin layer of alcohol over the heavy liquid causing the I^- to be removed slowly by diffusion into the upper layer; a somewhat more effective method in growing the hexagonal crystals was to place metallic silver in the saturated solution.

Investigators of the thermodynamic properties of silver iodide either ignored or were unaware of the low-temperature cubic and hexagonal structures existing at room temperature. A discrepancy of 200 to 300 calories in the standard heats of formation has been recognized since the work of Fischer (1912) and was discussed at length by Gerth (1921) who divided the existing data into two groups: calorimetric and electrochemical measurements. The excellent data of Gerke (1922), Lange and Shibata (1930), and Owen (1938) is nearly

useless because of their failure to characterize the structures of their samples.

Free energy and entropy data follow the same pattern of disagreement. Randall and Halford (1930) detected a free energy difference of 500 calories between a "precipitated" sample and a "hexagonal" sample of silver iodide. However, their "hexagonal" was prepared by HgI_2 digestion which, in the present work, is shown to be nearly pure low-temperature cubic; the "precipitated" form is invariably a mixture of cubic and hexagonal.

The stability relations between the four modifications of AgI is still somewhat confused. Bridgman (1915) was not aware of the low-temperature cubic form and his phase diagram shows the stability fields only for hexagonal, high-temperature, and high-pressure cubic. Bloch and Moller (1931) and Manson (1956) believed the sphalerite form to be stable below 120 to 135°C. at 1 atm. Majumdar and Roy (1959) were unable to prepare the sphalerite form and concluded that it does not exist - that it has "no range of thermodynamic stability". They further suggest that the wurtzite form is stable from 146.5°C. to room temperature, and that both the 120°C. transition of Manson (1956) and the 135-137°C. transition between the wurtzite and sphalerite modifications have no significance.

It appears then, in spite of the apparent satisfactory state of knowledge of silver iodide, that the thermodynamic properties and stability relations of its four crystalline

modifications are still unexplained and in many cases in direct disagreement.

2. Purpose of Study

This study is concerned with the structural and thermodynamic properties of silver iodide. The general purpose of this work is a critical evaluation of previously reported preparations and published thermodynamic data.

The following specific problems were studied:

1) Reproducible preparation and identification of the low-temperature cubic and hexagonal structures of silver iodide.
2) Determination of the stability relations between the low-temperature cubic and hexagonal structures by thermodynamic measurements.

3. Acknowledgements

Professor Clark C. Stephenson of the Department of Chemistry suggested the problem, supervised laboratory work, and directed the organization of this paper. Claus Wulff and Richard Orehotsky helped with several preparations. Paula Bordun assisted in the typing of the manuscript.

III. PREPARATIONS OF SILVER IODIDE

1. General Statement

Before considering the thermodynamic properties of silver iodide, it was necessary to confirm the reports of Wilsey (1922), Bloch and Moller (1931), and Kolkmeijer and van Hengel (1934) that both hexagonal and low-temperature cubic forms could be prepared, or the report of Majumdar and Roy (1959) that a sphalerite form of silver iodide does not exist. Both wurtzite and sphalerite forms were successfully prepared by three different methods for each form. X-ray diffraction methods were used to determine the structures of the preparations.

2. Identification of Preparations

X-ray Diffraction Apparatus - Crystal structures of the AgI preparations were determined by x-ray diffraction powder patterns. Powder photographs were taken in a Norelco Debye-Scherrer camera using the General Electric XRD-3 x-ray diffraction unit with CuK_{α} radiation at 45 kv., 15 ma. for 10 hours. A Norelco x-ray diffractometer and basic diffraction unit operated at 35 kv., 15 ma. was used for spectrometric powder patterns. The specimens were scanned at 1 degree 2θ per minute with a scale factor of 4, time constant of 4, and chart speed of $\frac{1}{2}$-inch per minute. To avoid confusion, the spectrometer data will be called "diffractometer patterns" as opposed to "powder patterns" for the photographs.

Specimen Preparation - The method of specimen preparation for x-ray diffraction patterns is important in silver iodide; both grinding and preferred orientation affect the results. Klug and Alexander (1954, p. 291) note that it is essential for satisfactory results that (1) the number of crystallites contributing to each reflection be sufficiently large to generate signals of reproducible intensity and that (2) preferred orientation of the crystallites be held to a minimum. Fortunately the crystal size of the silver iodide preparations is small enough to meet the requirements for smooth lines in powder patterns without grinding, and not too small to cause line broadening. Powder pattern specimens were prepared by rolling a vaseline-coated glass fiber in the sample; this technique provided uniform specimens and eliminated the necessity to grind the samples. Rotation of the cylindrical specimen in the Debye-Scherrer method increases the number of effective orientations and further reduces the problem of preferred orientation.

The diffractometer specimens were mounted on flat glass slides by eyedropper sedimentary fractionation of AgI suspended in amyl acetate, thus eliminating the larger crystallites or crystal aggregates. The technique proved most useful when it was desired to completely eliminate grinding. Gentle grinding under amyl acetate in an agate mortar had no observable effect on the 21-29° 2θ and 38-48° 2θ regions (see Tables 1 and 2 and compare Figures 1c and 2e) in which most of the diffractometer specimens were

scanned. Grinding under amyl acetate gave more uniform specimens and reliable data with only minor preferred orientation effects.

There is a marked change in the diffraction spectra when strong grinding is carried out in a dry agate mortar for several minutes. The AgI samples, especially hexagonal, turned bright yellow and formed large aggregate platelets where in contact with the mortar surface. The samples were then ground gently under amyl acetate to break up the large aggregates formed, and were mounted on the slides by sedimentary fractionation. Both diffractometer patterns and powder patterns indicate a conversion of hexagonal silver iodide to the low-temperature cubic form with considerable broadening of the lines. Cubic and hexagonal were prepared in this manner (AgI-5SG, AgI-16SG, and AgI-21SG - see Appendix 1); the effects of grinding are shown in Figure 1.

Structures of Crystalline AgI - All preparations of silver iodide were studied by x-ray diffraction. Samples exhibiting the clearest powder patterns were chosen for crystallographic data (Plate 1). The Miller indices, Bragg angles, interplanar spacings, and relative intensities are given in Tables 1 and 2 for AgI-17 (cubic - Plate 1a) and AgI-4 (hexagonal - Plate 1b). The structures of the high-temperature and high-pressure modifications are not a part of this study.

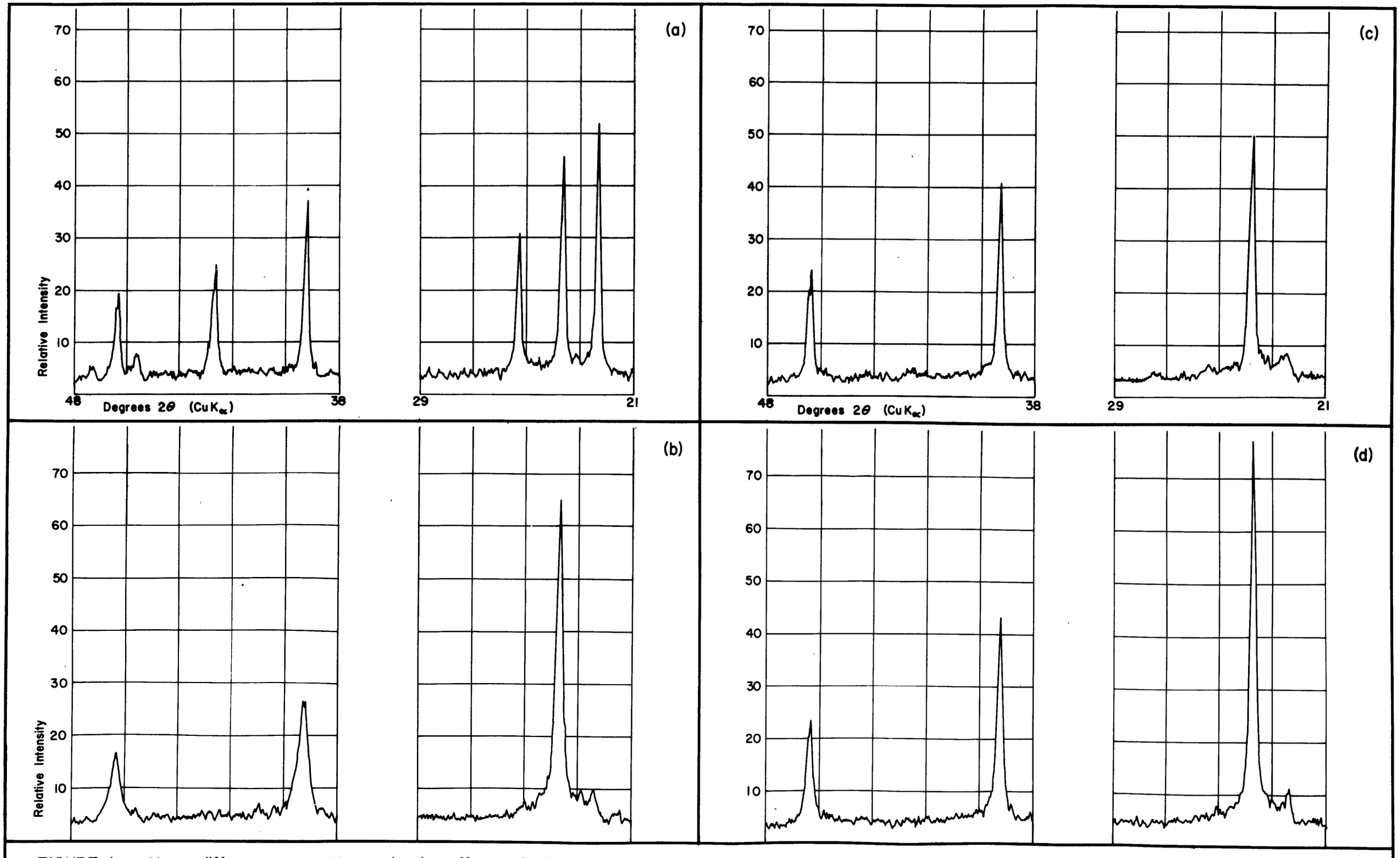


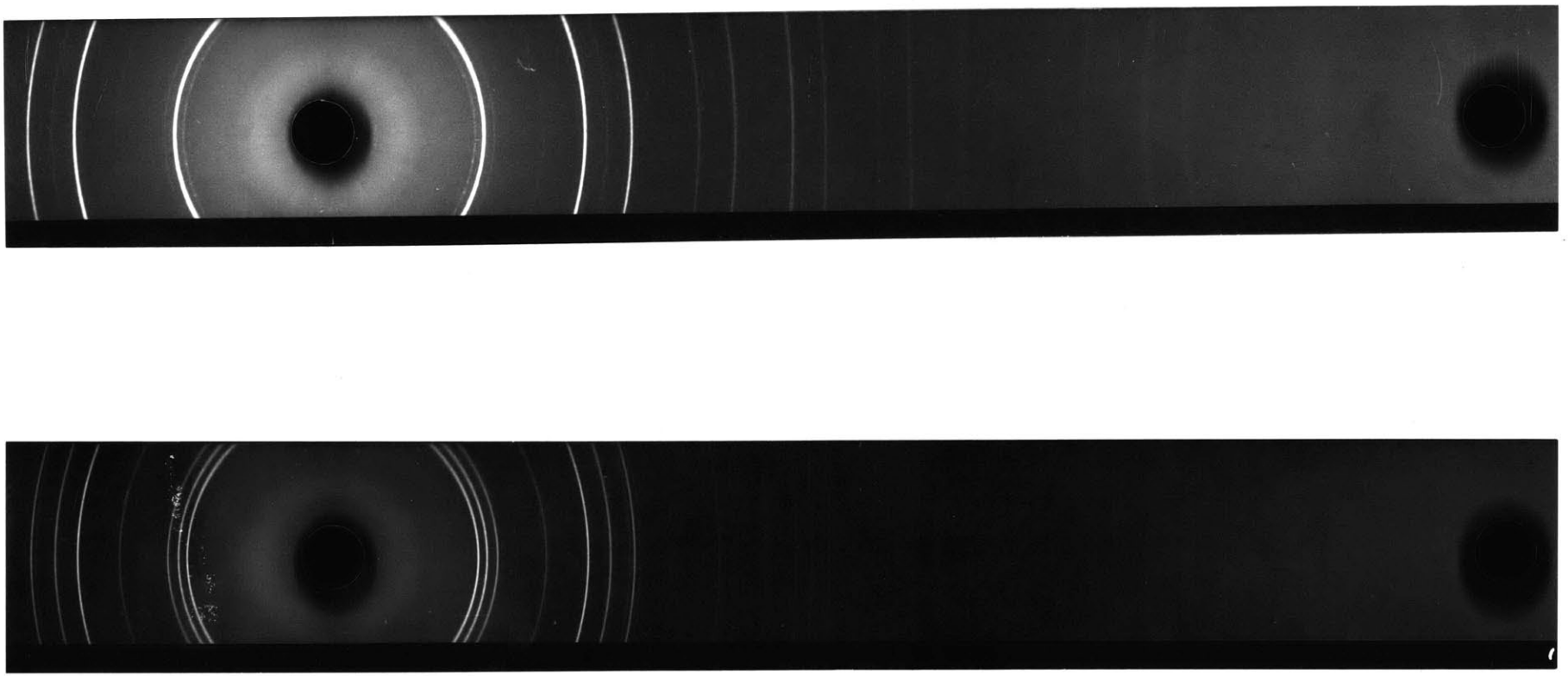
FIGURE 1. – X-ray diffractometer patterns showing effects of grinding hexagonal and cubic silver iodide.

a) AgI-21 hexagonal, unground

b) AgI-21SG, ground in dry agate mortar

c) AgI-16 cubic, unground

d) AgI-16SG, ground in dry agate mortar



a)

b)

PLATE 1. - X-ray diffraction powder photographs of a) the sphalerite structure (AgI-17) and b) the wurtzite structure (AgI-5) of silver iodide. (CuK_α radiation)

TABLE 1. - X-ray diffraction data for low-temperature cubic silver iodide (AgI-17).

h k l (cubic)	cm.	θ°	sin θ	d(Å)	I	a_o	h k l (hex.)
	4.46	11.17	.1937	3.980	w		100
111	4.73	11.85	.2054	3.753	vs	6.50	
	5.07	12.70	.2196	3.510	w		101
200	5.49	13.75	.2377	3.243	f	6.49	
	6.57	16.46	.2833	2.721	vw		102
	7.82	19.59	.3353	2.299	vs	6.50	
	8.53	21.37	.3643	2.116	w		103
311	9.25	23.17	.3943	1.960	s	6.50	
222	9.66	24.21	.4100	1.882	vvf	6.52	
	10.30	25.80	.4352	1.772	vvf		202
400	11.32	28.36	.4750	1.6229	m	6.492	
	11.87	29.74	.4960	1.554	vw		203
331	12.44	31.16	.5174	1.4899	ms	6.494	
420	12.78	32.02	.5302	1.4540	vf	6.502	
	13.28	33.27	.5485	1.403	vvf		105
422	14.19	35.55	.5814	1.3259	ms	6.496	
511	15.22	38.13	.6177	1.2480	m	6.485	
440	16.85	42.21	.6718	1.1475	w	6.491	
531	17.80	44.59	.7020	1.0981	m	6.496	
600	18.11	45.34	.7113	1.084	vvf	(6.50)	
620	16.50	41.34	.7508	1.0268	w	6.494	
533	15.55	38.96	.7776	.9914	w	6.501	
622	15.07	37.73	.7909	.975	vf	(6.47)	

h k l (cubic)	cm.	θ^o	sin θ	d(Å)	I	a_o	h k l (hex.)
444	13.84	34.67	.8225	.9373	w	6.494	
711	12.83	32.14	.8468	.9096	w	6.500	
	12.78	32.02	.8479	.9107			
642	10.97	27.48	.8872	.8682	w	6.498	
	10.87	27.23	.8892	.8684			
731	9.76	24.45	.9103	.8462	w	6.499	
	9.62	24.10	.9128	.8459			

Order of relative intensity: vs = very strong, s = strong, ms = moderately strong, m = moderate, w = weak, f = faint, vf = very faint, vvf = extremely faint.

TABLE 2. - X-ray diffraction data for hexagonal silver iodide (AgI-5).

h k l (hex.)	cm.	θ°	sin θ	d(Å)	I	h k l (cubic)
100	4.46	11.17	.1937	3.98	s	
002	4.74	11.87	.2057	3.75	s	
101	5.07	12.69	.2197	3.51	ms	
102	6.56	16.42	.2827	2.727	m	
110	7.83	19.60	.3355	2.298	s	
103	8.52	21.33	.3637	2.120	ms	
200	9.11	22.81	.3880	1.987	w	
112	9.27	23.21	.3941	1.956	m	
201	9.46	23.69	.4018	1.919	w	
202	10.40	26.04	.4390	1.757	w	
--	11.33	28.37	.4752	1.622	f	400
203	11.86	29.70	.4955	1.556	w	
210	12.32	30.85	.5128	1.5033	w	
--	12.47	31.22	.5183	1.4874	f	331
211	12.59	31.52	.5228	1.4746		
114	12.82	32.10	.5314	1.4507		
105	13.28	33.25	.5483	1.4060		
212	13.38	33.50	.5519	1.3968		
300	14.19	35.53	.5811	1.3266		
213	14.67	36.73	.5980	1.2891		
006,302	15.21	38.08	.6167	1.2500		
205,106	16.02	40.11	.6442	1.1967		
220	16.86	42.21	.6718	1.1475		

h k l (hex.)	cm.	θ^{o}	sin θ	d(Å)	I	h k l (cubic)
116,222	(17.82)	44.65	.7028	1.097		
215	(18.60)	46.60	.7266	1.061		
313	16.08	40.30	.7627	1.011		
402,216	14.72	36.86	.8001	.9635		
306,321	12.92	32.38	.8445	.913		
315	11.99	30.03	.8658	.8896		
	11.92	29.85	.8673	.8903		
410,118	10.97	27.47	.8872	.8689		
323	10.42	26.09	.8981	.8576		
	10.35	25.91	.8995	.8584		
412,226	9.76	24.44	.9104	.8461		
	9.62	24.09	.9129	.8458		

3. Experimental Procedures

Direct preparation of the cubic (sphalerite) form of AgI was accomplished by water dilution of a concentrated aqueous AgI and $AgNO_3$ solution and by digestion of HgI_2 in a dilute aqueous $AgNO_3$ solution, thus verifying Kolkmeijer and van Hengel's (1934) statement that excess silver ion favors precipitation of the cubic form. The hexagonal (wurtzite) form was precipitated by water dilution of a concentrated aqueous AgI and KI solution and by digesting metallic silver in an aqueous I_3^- solution, verifying that excess iodide favors the precipitation of the hexagonal form. Mixtures of cubic and hexagonal were obtained by addition of KI and $AgNO_3$ to $AgNO_3$ and KI solutions respectively. The cubic form can be completely converted to hexagonal by digestion in concentrated NH_4OH, and the hexagonal form can be converted to cubic by grinding in dry agate mortar as described above.

Reagent grade $AgNO_3$ (Mallinckrodt), AgI (Baker and Adamson), KI (Baker and Adamson), finely divided silver metal (Fisher), I_2 (Mallinckrodt), and HgI_2 (Merck) were used in the preparations. The Baker and Adamson AgI reagent used in most of the preparations has been identified as a mixture which is dominantly cubic; a Mallinckrodt AgI reagent, believed to be at least 10 years old, is the hexagonal form. All reactions were carried out at room temperature unless stated otherwise. The procedures of preparation are described below and the individual

preparations are tabulated in Appendix 1.

Procedure 1 - Precipitation of cubic AgI by dilution was carried out as follows:

1) One liter of 5.0 M $AgNO_3$ was warmed slightly on a steam bath and 48.5 grams of previously precipitated AgI was completely dissolved in the solution according to the solubility data of Hellwig (1900); no attempt was made to effect saturation. The AgI used consisted of 30 grams Baker and Adamson reagent; the remaining 18.5 grams consisted of 1) Mallinckrodt reagent, 2) hexagonal AgI prepared in 15 N NH_4OH, and 3) cubic AgI prepared by HgI_2 digestion. All samples of AgI were dry before dissolving. It was assumed that the original crystalline form had no effect on its ionic form in solution. The final solution was cooled to room temperature.

2) The first precipitation of AgI by this method was the rapid addition of 80 ml. of the above solution from a burette into 2 liters of distilled water ($AgNO_3$ = 0.2 M). The resulting precipitate (AgI-15) was vacuum filtered and dried with acetone. Analysis of its powder pattern (Plate 2c) showed the precipitate to be dominantly hexagonal with 11 new lines (Table 3) between 0 and 60° 2θ which were not found in either cubic or hexagonal patterns. It was proposed that during

TABLE 3. - $AgI \cdot AgNO_3$ impurities in preparation AgI-15 shown by x-ray diffraction data.

AgI XV 'new' lines		AgI XV-L 'new' lines		$AgI \cdot AgNO_3$ Diffraction Patterns		
				Powder	Diffractometer	
d(Å)	I	d(Å)	I	d(Å)	d(Å)	I
--	--	--	--	7.008	7.070	11
6.768	vw	--	--	6.742	6.804	67
--	--	--	--	4.572	4.588	31
--	--	--	--	4.287	(4.267)	(6.0)
--	--	--	--	4.111	--	--
3.870	vf	--	--	3.873	3.873	39
--	--	--	--	3.726	3.740	39
3.636	vf	--	--	--	--	--
3.434	vf	--	--	3.432	3.436	38
3.328	f	3.328	f	3.321	3.338	70
--	--	--	--	3.101	3.108	8
--	--	--	--	2.917	--	--
--	--	--	--	2.877	2.882	16
2.670	f	2.670	f	2.676	2.676	32
2.624	w	2.624	f	2.623	2.631	100
--	--	--	--	2.550	2.546	10
--	--	--	--	2.494	2.508	6
--	--	--	--	2.419	2.413	12
--	--	--	--	2.388	2.381	5
--	--	--	--	2.340	2.352	10
--	--	--	--	2.311	2.316	13
--	--	--	--	2.239	2.239	12

XV		XV-L		$AgI \cdot AgNO_3$		
d(Å)	I	d(Å)	I	d(Å)	d(Å)	I
2.207	f	2.207	vf	2.203	2.209	56
2.167	f	--	--	2.172	2.172	23
--	--	--	--	2.128	2.134	20
--	--	--	--	--	2.065	13
--	--	--	--	2.015	--	--
--	--	--	--	1.981	--	--
--	--	--	--	1.932	1.935	9
--	--	--	--	1.870	1.867	8
--	--	--	--	1.835	1.836	6
1.801	vf	--	--	1.803	1.806	6
--	--	--	--	1.763	--	--
1.714	vf	1.714	f	1.713	1.716	10
					1.713	9
--	--	--	--	1.663	1.668	9
					1.664	9
--	--	--	--	1.580	--	--
--	--	--	--	1.518	--	--

precipitation the solid phase first formed was one of the double salts of AgI and $AgNO_3$. These were reported by Hellwig (1900) as $AgI \cdot AgNO_3$, which precipitates in the region 1.215 M to 1.63 M $AgNO_3$; and $AgI \cdot 2AgNO_3$, which precipitates from $AgNO_3$ concentrations greater than 1.63 M. Both double salts (Plate 2a, 2b) were isolated by crystallization from $AgNO_3$ solutions saturated with AgI. The strongest lines of $AgI \cdot AgNO_3$ are in exact agreement with the 'new' lines in the AgI-15 pattern. Values for the Bragg angle θ and interplanar spacings have been calculated from diffractometer and powder patterns of $AgI \cdot AgNO_3$ and are presented in Table 3; analysis of the double salt structures is beyond the scope of this work. The preparation AgI-15 was 'leached' for 12 hours in 0.5 M $AgNO_3$ to cause the double salt impurities to disproportionate into AgI and $AgNO_3$ since $AgI \cdot AgNO_3$ is not the stable solid phase in 0.5 M $AgNO_3$. The number of 'new' lines decreased to 5 (Table 3). The same leached sample was returned to the flask containing 0.5 M $AgNO_3$ and leached for a month resulting in complete removal of the double salt (Plate 2d).

3) Since $AgI \cdot AgNO_3$ formed in the above dilution of 5.0 M $AgNO_3$ to 0.2 M, the dilution procedure was revised. The second precipitation was a drop by drop addition of 20 ml. of solution to a constantly

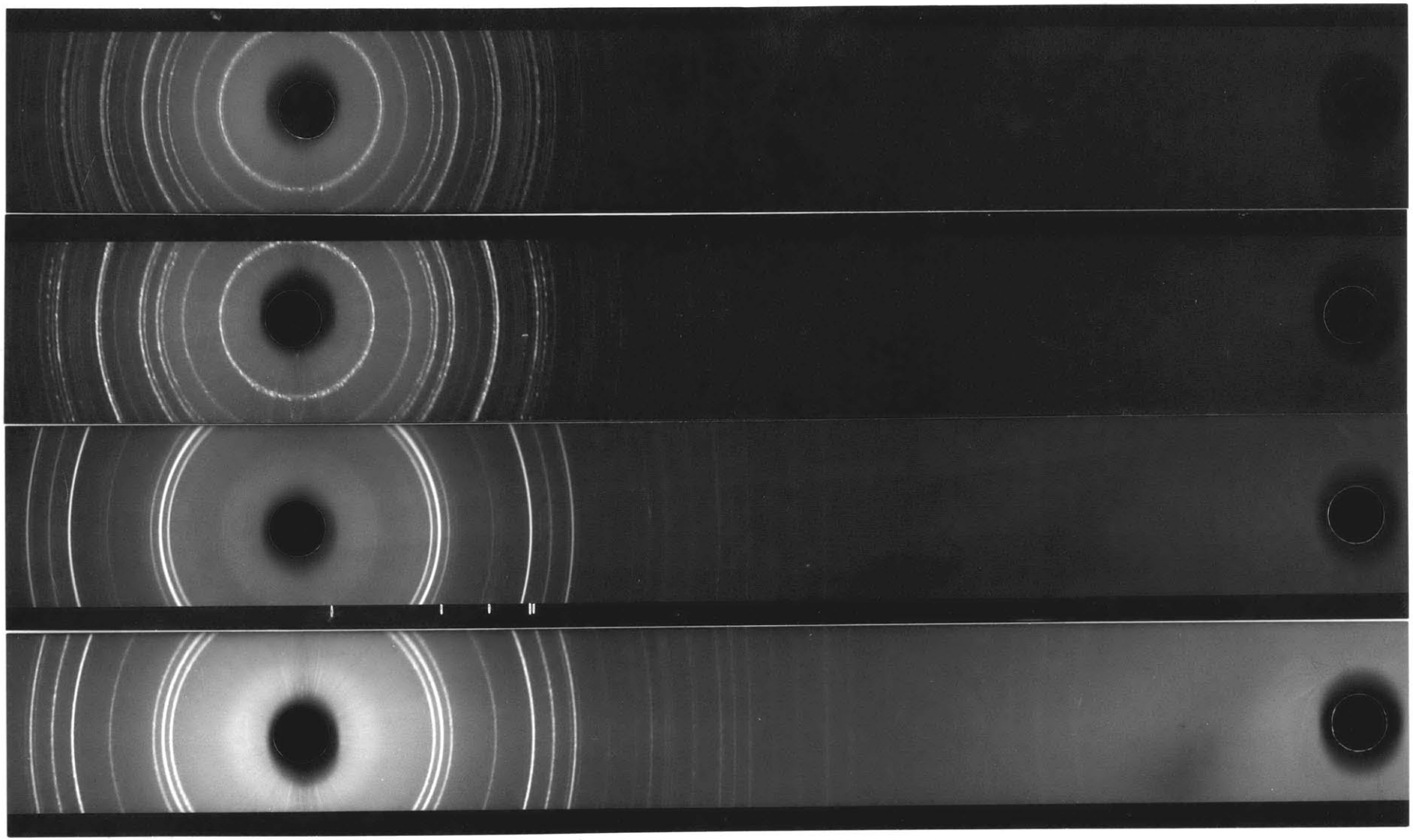


PLATE 2. - X-ray powder photographs of a) $AgI \cdot 2AgNO_3$, b) $AgI \cdot AgNO_3$, c) AgI-15, d) AgI-15LL.

stirred 2-liter volume of water ($AgNO_3$ = 0.05 M). The cloudy 2-liter aliquots containing the precipitate were stored in five 20-liter bottles for 4 days to allow the finely divided precipitate to settle out. The 39.7 grams of precipitate was filtered and dried with acetone yielding a somewhat fluffy, pale yellowish-gray precipitate (AgI-16) identified as the cubic form.

Manson (1955) prepared, by slow dilution of AgI dissolved in concentrated $AgNO_3$, two types of AgI: the first ground to pass 325 mesh identified as 88% cubic and the second unground identified as 94% cubic, the remainder in both cases being hexagonal. In the present work, a quantitative analysis of cubic and hexagonal was not attempted but powder and diffractometer patterns of AgI-16 appear to agree with the latter of Manson's preparations.

4) A similar solution was prepared in which 1 gram of reagent AgI was dissolved in 1 liter of 0.7 M $AgNO_3$. About 100 ml. of this solution was diluted to 700 ml. with water, and a fine gray precipitate formed, AgI-1, which was identified as cubic.

Procedure 2 - Precipitation of low-temperature cubic silver iodide by HgI_2 digestion was carried out as follows:

1) One liter of 0.1 M $AgNO_3$ was warmed to 90°C. on a steam bath and 0.11 moles (5 grams) of HgI_2

digested in the solution assuring an excess of silver ion according to the reaction:

$$\underline{HgI_2} + 2\ Ag^+ = 2\ \underline{AgI} + Hg^{++}.$$

The reaction proceeded very slowly and required 8 hours on the steam bath and occasional agitation to break up the small lumps of HgI_2 coated by AgI. The solution was then cooled to room temperature, filtered, and dried with acetone yielding a fluffy, bright yellow precipitate (AgI-3). While the solution cooled, small sparkling crystals of AgI formed and were later identified as hexagonal platelets in the precipitate; however, the precipitate formed was nearly pure cubic AgI.

2) Later preparations (AgI-23) by HgI_2 digestion showed that an increase in Hg^{++} concentration increases the amount of hexagonal in the precipitate. In order to prevent the formation of hexagonal crystals entirely, the solution was never allowed to cool below the temperature of the steam bath and at the end of digestion the solution was filtered while still hot (AgI-17). The most satisfactory and reproducible preparations (AgI-27) were made with 5 grams of HgI_2 in 1 liter of 0.1 M $AgNO_3$. Increasing HgI_2 to 10 grams and $AgNO_3$ to 0.15 M increased the number of hexagonal platelets in the precipitate (AgI-30).

Occasionally in these preparations, very small amounts

of undigested bright red HgI_2 are visible but its presence is not detectable in the powder patterns. The possibilities of contamination by the compound silver iodomercurate, Ag_2HgI_4, have been investigated. This yellow compound has both tetragonal (β) and cubic (α) structures between 25° and 100°C. and is usually prepared by digesting K_2HgI_4 in dilute solutions of $AgNO_3$ (Suchow and Keck, 1953). None of the x-ray diffraction lines reported by Ketelaar (1931 and 1934) or Frevel and North (1950) have been observed in any powder patterns. It appears that there is no problem of Ag_2HgI_4 contamination in preparing the low-temperature cubic silver iodide by HgI_2 digestion.

Procedure 3 - Precipitation of hexagonal silver iodide was accomplished by preparing a 1 liter solution of 3.0 M KI in which 60 grams of AgI was dissolved according to the solubility data of Hellwig (1900). The solution was diluted to 4 liters, vacuum filtered, and the precipitate dried with acetone to prevent discoloration. The precipitate obtained was in the form of fine-grained, dense white aggregates (AgI-21) and identified as the hexagonal form.

Procedure 4 - Hexagonal AgI was prepared by adding 1 gram of finely divided metallic silver to a dilute solution of solid I_2 dissolved in KI. Digestion required 12 hours at room temperature. The resulting precipitate (AgI-11) was identified as hexagonal. No trace of Ag in the powder pattern was observed.

Procedure 5 - Hexagonal AgI was prepared by digestion of

previously precipitated AgI in hot 15N NH_4OH followed by boiling off the NH_3 or evaporating the solution to dryness. This procedure afforded the purest hexagonal obtained during this work. Baker and Adamson AgI, dominantly cubic, was converted to hexagonal by this method (AgI-4, Plate 2b; and AgI-5) leaving only a faint trace of cubic in the powder pattern. The yellow AgI, when added to the hot NH_4OH solution, turned white indicating the formation of silver iodide hemiamine, $AgI \cdot \frac{1}{2}NH_3$. Concentrations of 1 to 3N NH_4OH did not convert cubic to hexagonal and possibly explains why Majumdar and Roy (1959) obtained a sphalerite-looking diffractometer pattern of a sample "treated with concentrated NH_4OH and evaporated to dryness at 110°C." It is proposed that the solid-solid conversion of cubic to hexagonal takes place through the hemiamine as an intermediate; however, the structure of the hemiamine has not been reported.

Effects of Heating - Samples of cubic and hexagonal silver iodide were sealed in dry flasks, and heated for 24 to 115 hours on a steam bath. Powder patterns of the heated samples were compared with unheated samples of the same preparations and no differences were observed in the line intensities. It appears that heating at 100°C. effects no change in the structure of either cubic or hexagonal silver iodide.

Preliminary x-ray data of samples heated in the 125° to 135°C. range used by Bloch and Moller (1931) did indicate a

partial conversion from the initial structure. Three diffractometer specimens mounted on glass slides (AgI-17, AgI-21SG, and AgI-21) were examined in the regions 21-29° and 38-48° 2θ and then placed in an oven set at 126± 2°C. for 70 hours. After heating, the samples were again examined with the diffractometer and the results are shown in Figure 2. Two cubic preparations, one prepared from HgI_2 and the other by grinding, have partially converted to hexagonal; and a hexagonal sample has apparently converted to the same mixture. All three samples show the same relative line intensities, the difference in peak heights between samples being accounted for by the number of crystallites contributing to the diffraction lines. The lines of the low-temperature cubic form prepared by grinding (AgI-21SG) have decreased in width.

4. Summary and Discussion of Results

The hexagonal and low-temperature cubic forms of silver iodide have been prepared and their structures identified by x-ray powder diffraction methods. The cubic form was prepared by H_2O dilution of a concentrated AgI-$AgNO_3$ aqueous solution, and by digesting HgI_2 in a dilute aqueous $AgNO_3$ solution. The hexagonal form was prepared by H_2O dilution of a concentrated aqueous AgI-KI solution, by digesting metallic silver in an aqueous triiodide solution, and by digesting solid AgI in hot concentrated NH_4OH.

X-ray diffraction patterns verify the previously

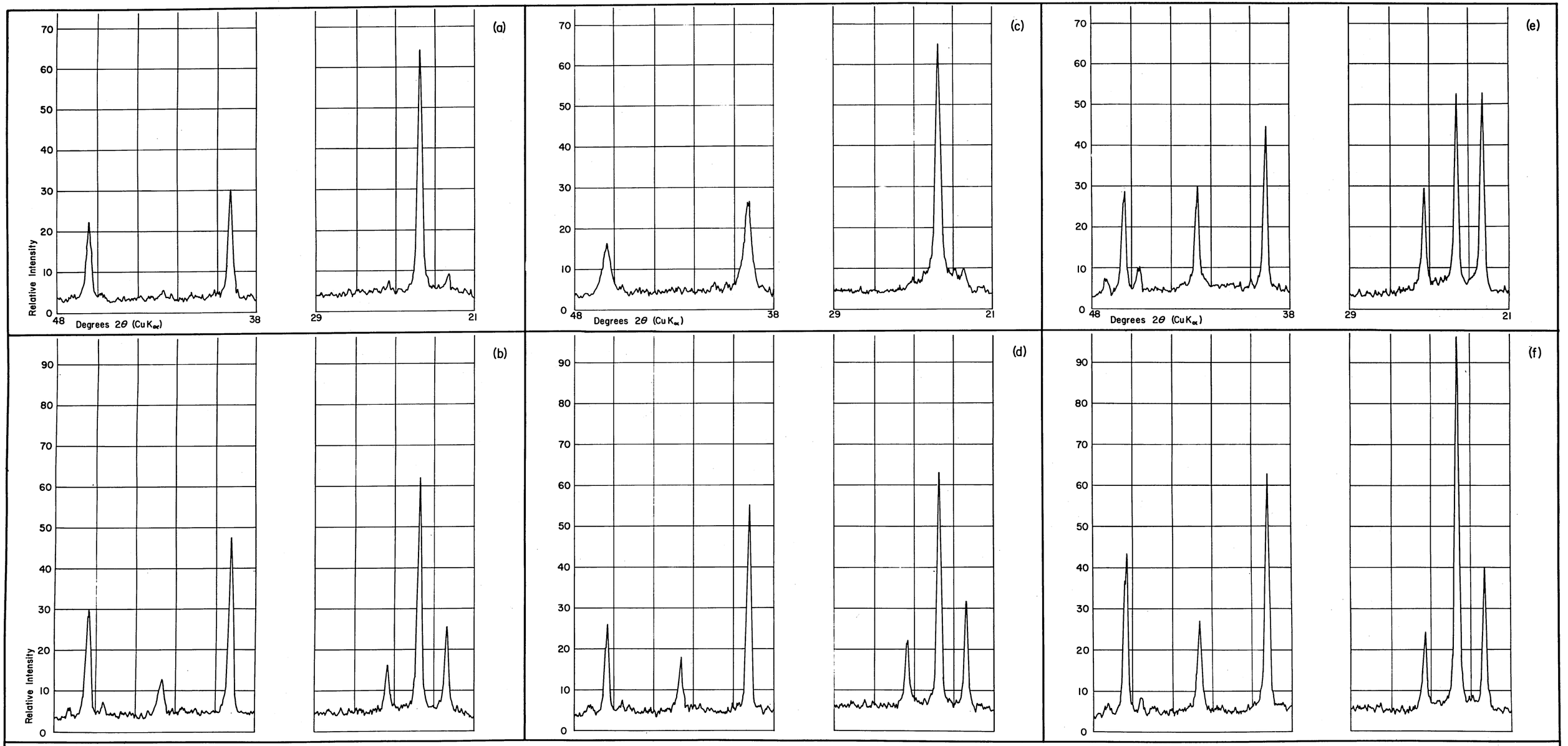


FIGURE 2. — X-ray diffractometer patterns showing effects of heating silver iodide powder specimens at 126°C for 70 hours.

a) AgI-17 cubic, unground.

b) AgI-17H, heated.

c) AgI-21SG, hexagonal ground in dry agate mortar.

d) AgI-21SGH, heated.

e) AgI-21G, hexagonal ground under amyl acetate.

f) AgI-21GH, heated.

reported wurtzite and sphalerite structures. The interplanar spacings and relative intensities agree with Bloch and Moller's (1930) data for both cubic and hexagonal and with the U. S. National Bureau of Standards' (1959) data for hexagonal. The faint (200), (222), (420), (600), and (622) lines have not been previously reported for the cubic form. The lattice constant $a_{o(ltc)}$ has been averaged for ten back reflection lines as 6.495 A. and is in reasonable agreement with Wilman's (1940) determination of 6.489 ± 0.005 A. obtained by electron diffraction.

Polytypes of the wurtzite and sphalerite structures of synthetic and naturally occurring ZnS and synthetic SiC have been well documented (Ramsdell, 1947; Frondel and Palache, 1950; Smith, 1955; Strock and Brophy, 1955; Evans and McKnight, 1959) but there is no clear evidence for wurtzite-sphalerite polytype structures in silver iodide. However, the interplanar spacings for the predicted 4H, 6H, 15R, and 21R simpler polytypes have been calculated and are tabulated in Appendix 2; the calculated 2H (wurtzite) and 3C (sphalerite) d values are in agreement with the values obtained for AgI-5 and AgI-17 in Tables 1 and 2.

Hexagonal silver iodide is converted to the cubic form by grinding in a dry agate mortar. Smith and Hill (1956) have reported similar inversion effects of hexagonal ZnS to cubic ZnS by impact grinding. A sample of 100% hexagonal ZnS (wurtzite) was converted to 61% cubic and a sample 93% cubic ZnS (sphalerite) was converted to 76% cubic. They

randomized by deformation faulting during grinding and that much of the broadening is due to particle size effect. When AgI is ground, significant line broadening is observed only in the case of the hexagonal samples (Figure 1); the cubic patterns appear unchanged except in the region 22-24° 2θ where slight broadening is observed. Burns and Bredig (1956) converted calcite, which is stable at normal temperature and pressure, to metastable aragonite by grinding the crystals in a mechanical mortar for intervals up to 38 hours. The minimum pressure required at room temperature to effect this conversion was calculated to be between 3920 and 4600 kg./cm.^{2} The fact that the opposite transition does not occur when the hydrostatic pressure is released suggested that shearing stress and deformation faulting may be involved. It is interesting to note that grinding PbO, ZnS, and CaC_2 produces the more stable form at room temperature whereas $CaCO_3$ and AgI are converted into the less stable form. Burns and Bredig also found that heating the ground $CaCO_3$ to 450°C., which is above the 1 atm. calcite-aragonite transition temperature, reconverted all the $CaCO_3$ into calcite. In a similar manner AgI-21SG (figures 2c and 2d) was partially reconverted to the hexagonal form when heated for 70 hours at 126°C. A decrease in the line broadening effect was also observed. However, in the case of silver iodide, heating probably increases the <u>rate</u> of metastable to stable reconversion rather than passing through a hexagonal-low-temperature cubic transition point.

IV. THERMODYNAMIC PROPERTIES

1. General Statement

In view of the anomalous thermodynamic data of silver iodide which, in many cases, exceeds the limits of experimental error, it is desirable to know the free energy, heat content, and entropy differences for the change in state

AgI (low-temperature cubic) = AgI (hexagonal).

These effects are small since the difference in structures is the only difference between hexagonal and cubic closest packing of the iodides, but may be on the order of several hundred calories, thus affording a possible explanation for the disagreement among the thermochemical data. Several methods to detect these differences are possible:

1) Heat of formation difference by heats of solution measurements $\Delta H = \Delta H(\text{hex}) - \Delta H(\text{ltc})$.
2) Free energy difference (ΔF) by cell measurements in which Ag-AgI(hex) and Ag-AgI(ltc) electrodes are used.
3) ΔH by temperature coefficient of the above cell.
4) ΔF by solubilities of the two forms in KI, $AgNO_3$, or KCN.

The heats of solution measurements are described below. The latter three methods have been briefly investigated but no reliable data are available at present.

2. Heats of Solution

Apparatus and Procedure - The heats of solution reactions were carried out in the solution calorimeter described by Shoemaker and Garland (1957) which is a Dewar flask containing a motor-driven stirrer, a heating coil of 6.015-ohms resistance, and a Beckmann precision thermometer readable to 0.001°C. The accuracy of the temperature differences is probably no greater than ±0.005°C. For determining the heat capacity, an electric current of about 1.5 ampere was passed through the heating coil during a known time interval. The magnitude of the current was measured as a function of time by the potential difference developed across a 0.153-ohm standard resistance with a Leeds and Northrup potentiometer.

600 ml. of 5.00 M KI was equilibrated in the calorimeter for 30 minutes and the samples of AgI (15.0000 ± 0.0007 g.) were introduced through a funnel within 15 seconds of the recorded time. The heats of solution were measured in the temperature range of 22-27°C.; the temperature of samples was determined before each run by inserting the thermometer directly into the sample.

Results - The change in state occurring in the calorimeter may be represented by the following equation:

$$15g.\ AgI(\text{ltc or hex},\ t_2) + 600ml.\ 5M\ KI(t_1) + \text{calorimeter}(t_1) = \text{solution}(t_3) + \text{calorimeter}(t_3),\ \Delta H_1 = 0.$$

The isothermal heat of solution at t_1 is obtained by adding

the following equations to that given above:

15g. AgI(ltc or hex, t_1) = 15g. AgI(ltc or hex, t_2), $\Delta H_2 = C_{AgI}(t_2-t_1)$,

solution and calorimeter(t_3) = solution and calorimeter(t_1), $\Delta H_3 = C_{sc}(t_1-t_3)$.

The heat capacity of 15g. AgI, C_{AgI}, was taken as 13.6 x (15/234.8) cal./deg. (Kelley, 1949, p. 160) and the heat capacity of the solution and calorimeter, C_{sc}, found experimentally was 470 cal./deg.

Representative data for one of the measurements of the heat of solution of AgI(hex) are summarized below:

$t_2-t_1 = -1.35^\circ$, $\Delta H_2 = -1.35 \times C_{AgI} = -1.2$ cal.

$t_1-t_3 = -0.278^\circ$, $\Delta H_3 = -0.278 \times 470 = -130.7$ cal.

$$\Delta H \text{ (per mole of AgI)} = (0 - 1.2 - 130.7) \times \frac{234.8}{15} = -2{,}063 \text{ cal.}$$

The accuracy of the results is largely dependent on the measurement of t_1-t_3. Conditions were chosen to make this quantity as large as possible, and the liberal estimate of $\pm$50 cal. in the final values of the heats of solution is based in part on the assumption of a possible error of 0.005° in t_1-t_3. ΔH_2 was never more than a few percent of ΔH_3.

The results of eleven measurements of silver iodide preparations are given in Table 4 on the following page:

TABLE 4. - Silver iodide heats of solution.

Sample	Preparation	Structure	ΔH, cal./mole
AgI-27-1	HgI_2	l.t. cubic	-2290
AgI-27-2	HgI_2	l.t. cubic	-2430
AgI-23	HgI_2	l.t. cubic	-2360
		Average	-2360 ± 50
AgI-16-1	$AgNO_3$ dil.	l.t. cubic	-2220
AgI-16-2	$AgNO_3$ dil.	l.t. cubic	-2230
		Average	-2230 ± 50
AgI-25-1	conc. NH_3	hexagonal	-2060
AgI-25-2	conc. NH_3	hexagonal	-2100
AgI-28	conc. NH_3	hexagonal	-2090
		Average	-2080 ± 50
AgI-21-1	KI dil.	hexagonal	-2110
AgI-21-2	KI dil.	hexagonal	-2110
AgI-21-3	KI dil.	hexagonal	-2180
		Average	-2130 ± 50

3. Summary and Discussion of Results

The determination of the heat of solution of AgI(hex) prepared in two different ways are in satisfactory agreement, and -2110±50 cal. is selected for the heat of solution of this modification. The difference between the heats of solution of the two preparations of low-temperature cubic

silver iodide appears to be greater than the experimental error, although more accurate measurements will be necessary to establish this effect without doubt. For the present, the heat of solution of the cubic modification will be taken as -2230±50 cal. because the preparations from $AgNO_3$ solutions are comparable in particle size to the hexagonal samples and are free from contamination by HgI_2.

For the change in state

$$AgI(ltc) = AgI(hex), \quad \Delta H = -110 \text{ cal.}$$

If the results for the other preparation of the cubic modification are used, $\Delta H = -250$ cal. The difference in the heat content between the two structures is small but definite, and there is no question about the sign.

There are no comparable thermal data on AgI in the literature; indeed, these are the only thermodynamic measurements on samples of AgI in which the crystalline form is characterized. Nevertheless, it is of interest to summarize the more reliable data on the standard heat of formation of silver iodide:

ΔH_f, cal.	Reference
-14,820 ± 300	Fischer, (1912)
-15,100 ± 100	Braune and Koref, (1914)
-15,130 ± 100	Taylor and Anderson, (1921)
-14,980 ± 100	Webb, (1925)
-14,813 ± 30	Gerke, (1922)
-15,050 ± 50	Lange and Shibata, (1930)
-15,340 ± 30	Bertram and Roth, (1937)
-14,820 ± 30	Owen and Brinkley, (1938)

The above investigators were either unaware of the existence of the cubic and hexagonal modifications of silver iodide or ignored their existence, recalling that Wilsey (1922) reported the existence of the cubic form and that the mineral iodyrite had long been known to be hexagonal. The first four investigators listed above used precipitated silver iodide, which is invariably a mixture of hexagonal and cubic, for their calorimetric studies. The results of Gerke (1922) and Owen and Brinkley (1938), which are in excellent agreement, are derived from the temperature coefficients of cells using Ag-AgI electrodes. The electrode is apparently reversible and reproducible, but there is ambiguity about the form of silver iodide that controls its potential. Lange and Shibata (1930) measured the heat of precipitation of silver iodide, and their very accurate calorimetric measurements then refer to an unknown mixture of hexagonal and cubic silver iodide. Bertram and

Roth (1937) measured the heat of reaction of metallic silver with triiodide ion which leads to the formation of hexagonal silver iodide (AgI-II). Unfortunately, their results usually have an error of $\pm$300 cal. rather than $\pm$30 that they give.

There does seem to be a real difference between the heat contents of precipitated silver iodide and the silver iodide controlling the cell measurements:

AgI (electrodes) = AgI (precipitate), ΔH = -230 cal.

This difference is of the same order of magnitude as that found in this study. Perhaps the electrodes used by Gerke (1922) and Owen and Brinkley (1938) were controlled by the cubic modification whereas the precipitated forms were predominantly hexagonal. However, the failure of these investigators to characterize their samples makes any attempt to interpret their results speculative.

The calorimetric measurements discussed above are not sufficient to establish the relative stabilities of the hexagonal and low-temperature cubic modifications of silver iodide without additional data. However, this information may be combined with the qualitative evidence of Bloch and Moller (1931) and of Manson (1956) that low temperature cubic converts to hexagonal at temperatures between about 120° and 146°C. Hence, for the change in state

AgI(ltc) = AgI(hex), ΔF is negative ($T \sim 419°K$) and ΔH = -110 cal. If ΔC_p is assumed to be zero, ΔH

and ΔS are independent of T, and we may write

$$\Delta F_T = -110 - T\Delta S.$$

Since ΔF is negative at 419°K., $\Delta S \geq -0.26$ entropy units and ΔF must remain negative at all temperatures lower than 419°K. Hence, the sphalerite modification is metastable with respect to the hexagonal form up to 146°C. where the hexagonal converts to the high-temperature cubic form.

This is a surprising result. Both Bloch and Moller and Manson believed that sphalerite form was the stable modification at low temperatures. The former authors gave a transition temperature of approximately 135°C. and Manson placed the transition at 120°C. However, Bloch and Moller never observed the conversion of hexagonal to low temperature cubic and their arguments for a transition temperature at about 135°C. are not convincing. Manson does report a partial conversion of hexagonal to cubic at room temperature after one year, but he does not give sufficient experimental evidence pertaining to this observation for an adequate criticism.

Bloch and Moller (1931) in the same paper present far more convincing evidence with x-ray diffraction patterns that both hexagonal and low temperature cubic converts to high-temperature cubic at 146°C. within 0.1° of each other. Thus,

$$AgI(hex) = AgI(htc),\ \Delta F_{419^oK} = 0,\ cal.;$$

$$AgI(ltc) = AgI(htc),\ \Delta F_{419^oK} = 0 \pm 0.3\ cal.;$$

and, $$AgI(ltc) = AgI(hex),\ \Delta F_{419^oK} = 0 \pm 0.3\ cal.$$

At 146°C., one-tenth of a degree corresponds to 0.3 cal. in ΔF for the conversion of low temperature cubic to high temperature cubic. The exact transition temperature for low temperature cubic to hexagonal can be several degrees lower than 419°K. only if ΔS is very small and positive. However, the calorimetric results preclude this possibility because ΔS is negative if the transition temperature is less than 419°K. If the transition temperature is taken as 419°K, then

$$\Delta F_T = -110 + 0.26\ T$$

$$\text{for AgI(ltc)} = \text{AgI(hex)}$$

The thermodynamic argument is more easily seen from Figure 3 which represents $\Delta F = F - F_{hex}$ as a function of temperature. The curves representing $F_{htc}-F_{hex}$ and $F_{hpc}-F_{hex}$ are approximate representations of the data of Bridgman (1915). On these curves are placed two curves for the low-temperature cubic. One of these corresponds to the phase diagram of Bloch and Moller whereas the other represents the equation $\Delta F_T = 110 - 0.26\ T$ for AgI(hex) = AgI(ltc). The different slopes of these lines reflect the fact that ΔS is positive for one curve and negative for the other, and for this reason the Bloch and Moller curve is rejected.

Bloch and Moller felt that grinding converted the metastable to the stable phase but the present interpretation requires this conversion to be from stable hexagonal to metastable low-temperature cubic as in the case of grinding

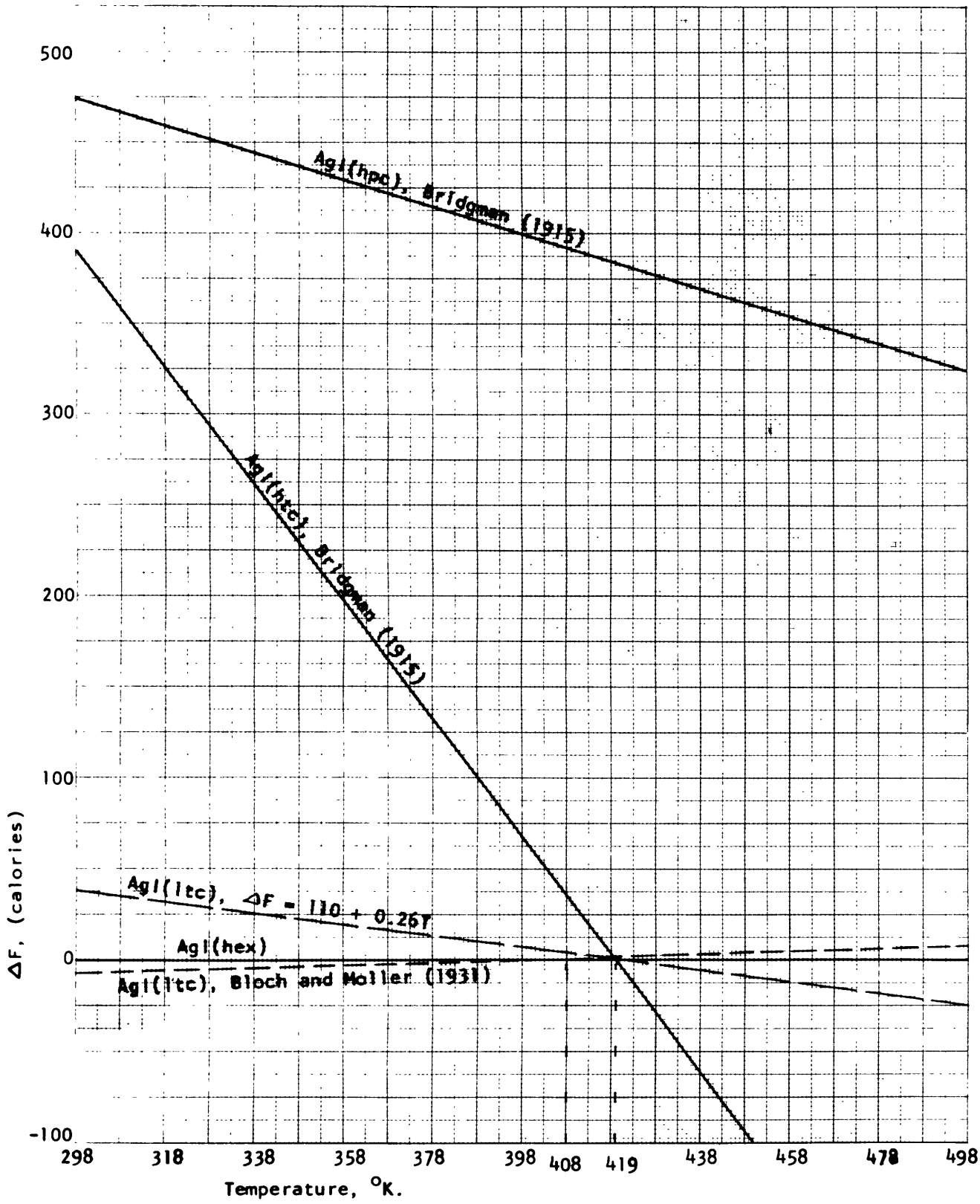


FIGURE 3.- $\Delta F = (F - F_{hex}) = f(T)$ for AgI(hpc), AgI(htc), AgI(hex) after Bridgman (1915); AgI(ltc) after Bloch and Moller (1931); and AgI(ltc), $\Delta F = 110 + 0.26T$, this report.

calcite to aragonite (Burns and Bredig, 1956). In the case of silver iodide, it appears that the hexagonal is first converted to the high-pressure cubic which then reverts to metastable low-temperature cubic under the conditions of grinding.

V. CONCLUDING STATEMENT

Cubic silver iodide of the sphalerite structure has been prepared by three different methods; x-ray diffraction data confirm the reports of Wilsey (1922), Bloch and Moller (1931), and Kolkmeijer and van Hengel (1934) of its existence. The mercuric iodide preparation of the low-temperature cubic form has not been previously reported although Randall and Halford (1930) prepared "hexagonal" AgI by this method. They probably did prepare the hexagonal form since the purity of the cubic form is extremely sensitive to temperature and mercuric ion concentration during preparation. Majumdar and Roy (1959) prepared AgI by eleven different methods. In addition to the effects of grinding, two of these preparations should have afforded the low-temperature cubic modification. However, they state:

> "The first general and surprising result is, therefore, that AgI cannot be synthesized in the pure cubic sphalerite structure in any reproducible manner by methods previously suggested.... There is no experimental proof for the existence of a true sphalerite form of AgI."

In this investigation no preparation of the sphalerite structure has been 100 percent of that form. The x-ray powder patterns always show faint characteristic lines of the hexagonal wurtzite structure. If 100 percent purity is required to verify the existence of a compound, the statements of Majumdar and Roy are correct. However, it may be argued that the lines representing the hexagonal 'impurities' are, in fact, an indication of polytypes of the

wurtzite structure in AgI, but no other lines predicted for the simpler polytypes have been found in any of 30 silver iodide powder patterns. It is therefore concluded that only the simple wurtzite and sphalerite structures have been prepared under the present experimental conditions and that the faint hexagonal lines represent impurities in the low-temperature cubic preparations.

The measured difference in heat content for the change in state AgI(ltc) = AgI(hex) is on the order of -110 to -250 cal./mole. This difference provides a reasonable explanation for the uncertainties of several hundred calories in the published thermodynamic data for ΔH_f and ΔF_f. It is the negative sign of this ΔH which permits a strong thermodynamic argument in favor of the stability of the hexagonal form of silver iodide at all temperatures below 146°C. under one atmosphere pressure. However, the relative stability of the wurtzite and sphalerite structures of silver iodide is still unsettled since there is no data available for the difference in free energy between the two modifications. Randall and Halford report a difference of 500 calories in ΔF calculated from solubility measurements on two AgI preparations. The observations of Bloch and Moller (1931) and Manson (1956) that the low-temperature cubic converts to hexagonal between 120 and 135°C. and the heating effects shown in Figure 2 are still unexplained. The present heat of solution data require that these effects be controlled by the rate of solid-state conversion from

metastable cubic to stable hexagonal rather than the conversion of stable cubic to stable hexagonal. The fact that the reverse transition has not been observed, except under conditions of grinding; and that the transition is a 15 degree range, further supports the stability argument presented here.

VI. SUGGESTED WORK

In view of the conclusions presented above, the following studies are suggested to further clarify some of the unexplained and anomalous properties of crystalline silver iodide:

1) The heats of solution should be refined to obtain greater precision and more reproducible results. These measurements should agree for at least two preparations of the sphalerite structure of AgI. Particle size may have some bearing on these measurements.

2) The free energy difference between the cubic and hexagonal forms can be determined by solubility measurements and cell measurements in which Ag-AgI(hex) and Ag-AgI(ltc) electrodes are used; $\triangle H$ can be determined from the temperature coefficient of the cell.

3) Further x-ray diffraction studies are necessary to explain the anomalous line intensities often obtained; the possible existence of wurtzite-sphalerite polytypes has not been eliminated. The experiments of Bloch and Moller and Manson on the cubic-hexagonal transition between 120 and 135°C. should be repeated; the effects of heating diffractometer specimens in the range 100 to 150°C. may explain their results.

4) Finally, the standard free energies and heats of formation should be redetermined on samples of silver iodide in which the crystal structures are known.

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APPENDIX 1. - Summary of Preparation and Identification Data

Compound	Method of Preparation	Dominant Crystalline Form
AgI-1	100 ml. of 1 g. AgI dissolved in 1000 ml. 0.7 M $AgNO_3$ diluted to 700 ml. with water.	l.t.c.
AgI-3	Digestion of 5 g. HgI_2 in 1000 ml. 0.1 M $AgNO_3$ at 95°C.	l.t.c.
AgI-3SG	AgI-3 ground strongly in dry mortar.	l.t.c.
AgI-4	AgI digested in 15N NH_4OH.	hex.
AgI-5	AgI boiled to dryness at 95°C. in 15N NH_4OH.	hex.
AgI-7	2 g. AgI in 100 ml. cold 3N NH_4OH.	l.t.c.
AgI-8	2 g. AgI in 100 ml. 3N NH_4OH boiled to dryness at 95°C.	l.t.c.
AgI-9	25 ml. 1.74 M KI added to 20 ml. 2.0 M $AgNO_3$.	mixture
AgI-11	Finely divided Ag metal digested in I_2 dissolved in KI.	hex.
AgI-12	AgI-Mal. heated in dry flask (100°C.) 114 hrs.	hex.
AgI-13	AgI-B.&A. heated in dry flask (100°C.) 45 hrs.	l.t.c.
AgI-14	AgI-3 heated in dry flask (100°C.) 24 hrs.	l.t.c.
AgI-15	AgI in 5.0 M $AgNO_3$, 80 ml. diluted in 2000 ml. water.	hex.
AgI-15L	AgI-15 leached 12 hrs. in 0.5 M $AgNO_3$.	hex.
AgI-15LL	AgI-15 leached 32 days in 0.5 M $AgNO_3$.	hex.

Compound	Method of Preparation	Dominant Crystalline Form
AgI-16	AgI-8 in 5.0 M $AgNO_3$, 920 ml. diluted to 100 liters.	l.t.c.
AgI-16G	AgI-16 gently ground under amyl acetate in mortar.	l.t.c.
AgI-16SG	AgI-16 strongly ground in dry mortar.	l.t.c.
AgI-17	Same as AgI-3 filtered from hot solution.	l.t.c.
AgI-17G	AgI-17 gently ground with amyl acetate in mortar.	l.t.c.
AgI-17H	AgI-17 heated 70 hrs. at 126°C.	mixture
AgI-21	60 g. reagent AgI dissolved in 1000 ml. 3.0 M KI diluted to 4000 ml. with water.	hex.
AgI-21G	AgI-21 gently ground with amyl acetate in mortar.	hex.
AgI-21SG	AgI-21 strongly ground in dry mortar.	l.t.c.
AgI-21GH	AgI-21G heated 70 hrs. at 126°C.	mixture
AgI-21SGH	AgI-21SG heated 70 hrs. at 126°C.	mixture
AgI-22	50 g. AgI dissolved in 2000 ml. 5.0 M KI diluted to 5000 ml. with water.	hex.
AgI-23	50 g. HgI_2 digested in 2000 ml. 0.4 M $AgNO_3$ at 90°C.	l.t.c.
AgI-25	28 g. AgI-B.&A. digested in 300 ml. hot 15N NH_4OH.	hex.
AgI-27	10 g. HgI_2 digested in 2000 ml. 0.1 M $AgNO_3$ at 90°C.	l.t.c.
AgI-28	Same as AgI-25.	hex.
AgI-29	AgI-23 digested in hot 15N NH_4OH.	l.t.c.

Compound	Method of Preparation	Dominant Crystalline Form
AgI-30	20 g. HgI_2 digested in 2000 ml. 0.15 M $AgNO_3$ at 90°C.	l.t.c.
AgI-B.&A.	AgI - Baker and Adamson reagent (M.I.T. accession #7375-x).	l.t.c.
AgI-Mal.	AgI - Mallinckrodt reagent.	hex.

APPENDIX 2. - Calculated AgI Polytype Diffraction Spectra

INDICES			Polytype diffractions in 3 degrees of intensity: s = strong, m = medium, w = weak						
Cubic h k l	Hex. hk·l	d(A)	2H .000	9R .333	4H .500	15R .600	6H .667	21R .714	3C 1.00
	10.0	3.974	s		m				
	10.1/15	3.966				w			
	10.2/21	3.955						w	
	10.1/9	3.947		m					
	10.2/15	3.938				w			
	10.1/6	3.917					m		
	10.4/21	3.896						m	
	10.2/9	3.871		w					
	10.5/21	3.855						m	
	10.1/4	3.846			w				
	10.4/15	3.828				m			
111	00.2 10.1/3	3.748	m	m	m	s	s	s	s
	10.8/21	3.687						w	
	10.4/9	3.598		m					
	10.7/15	3.565				m			
	10.10/21	3.548						w	
	10.1/2	3.515	s		m		w		
	10.11/21	3.476						w	
	10.8/15	3.461					m		
	10.5/9	3.427		m					

Cubic h k l	Hex. hk·l	d(A)	2H .000	9R .333	4H .500	15R .600	6H .667	21R .714	3C 1.00
	10.13/21	3.324						w	
200	10.2/3	3.246				w	w	w	w
	10.11/15	3.139				w			
	10.3/4	3.112			w				
	10.2	2.727	m		w				
	10.11/9	2.430		w					
	10.25/21	2.409						w	
	10.5/4	2.396			w				
	10.19/15	2.374				w			
220	11.0 10.4/3	2.295	s	m	m	s	s	s	s
	11.2/7	2.261						w	
	11.1/3	2.248		w					
	11.4/7	2.165						m	
	11.3/5	2.155				m			
	11.2/3	2.124		m					
	10.3/2	2.116	s		m		w		
	11.5/7	2.103						w	
	11.4/5	2.062				w			
	11.6/7	2.033						w	
	20.0	1.989	w						
	20.1/6	1.979					w		
	20.4/15	1.967				w			
	11.2								
311	10.5/3	1.959	m	m	m	s	s	m	s
	20.1/3								

Cubic h k l	Hex. hk·l	d(A)	2H .000	9R .333	4H .500	15R .600	6H .667	21R .714	3C 1.00
	20.4/9	1.936		w					
	20.7/15	1.929				w			
	20.1/2	1.920	m		m		w		
	20.8/15	1.913				w			
	20.5/9	1.907		w					
	10.7/4	1.887			m				
222	00.4 20.2/3	1.873	w	w	w	w	w	w	w
	20.2	1.757	w		w				
	20.5/4	1.657			w				
400	20.4/3	1.624				w	w	w	w
	20.3/2	1.556	m		m		w		
	21.0	1.502	w	w	w	w	w	w	
	10.7/3								
331	20.5/3	1.490					m		m
	21.1/3								
	21.1/2	1.474	w		w		w		
420	11.4 21.2/3	1.452		w		w	w	m	m
	10.5/2	1.403	w		w				
	10.8/3								
422	21.4/3	1.326	w	m	w	m	s	s	s
	30.0								
	21.3/2	1.287	m		w		w		

Cubic h k l	Hex. hk·l	d(A)	2H .000	9R .333	4H .500	15R .600	6H .667	21R .714	3C 1.00
	00.3								
333	20.7/3	1.250	w	w	w	w	m	m	m
511	21.5/3								
	30.2								
	20.5/2	1.197	w		w				
440	20.8/3	1.148	w	w	w	w	m	m	m
	22.0								
531	11.3	1.098	w	m	m	m	m	m	m
	31.1/2	1.090	w						
	21.5/2	1.062	m		w				
620	21.8/3	1.027		w		w	m	m	m
	31.3/2	1.009	m		w		w		

The spacing of most of the reflecting planes of the simpler possible polytype structures of AgI are shown above. These are calculated from $d(A)_{AgI} = 2.0107\ d_{ZnS}$ after the data of Smith (1955). The terminology which has become accepted designates cubic (ltc) as 3C and hexagonal as 2H. The polymorphs 2H and 3C are end members of the series. Intervening polytypes have hexagonal or trigonal symmetry and are said to be polytypes of the hexagonal end member. The number of AgI layers per cell is given by a number (2, 4, 6, 9, 15,...) followed by H or R indicating hexagonal or rhombohedral symmetry. The numbers (.000, .333, .500,...) give the ratio of cubic to hexagonal packing.