High-Pressure Polymorphs in the Silver Iodide Phase Diagram

Abstract. *A good x-ray diffraction pattern has been obtained for the new phase of silver iodide stable in the vicinity of 3 kilobars at room temperature. A stability diagram of the six phases of silver iodide is presented to show the probable position of the narrow stability field of this phase. The x-ray diffraction data indicate that the cell symmetry of the new phase is probably orthorhombic.*

It now appears that silver iodide can exist in at least six polymorphic modifications. At room temperature and atmospheric pressure, that the stable form is hexagonal wurtzite type (II, Fig. 1) is evident from the careful work of Burley (1). This phase is readily converted, by grinding in a mortar or by pressing, to a metastable sphalerite-type form (II′), which at temperatures above 80°C (and below 146°C) is observed to transform spontaneously and irreversibly to the hexagonal wurtzite-type modification. Moreover, it seems likely that below 80°C the wurtzite-type form is the stable one, although at these low temperatures the sphalerite-type form persists indefinitely. For this reason Majundar and Roy (2) conclude that a true stability region of phase II′ does not exist. Here is a case in which not only the densities but also the lattice energies (3) are nearly the same at room temperature. Apparently the free energies are also so similar that it is academic to label one form as the stable one, and the other metastable.

Above 146°C phase II inverts to a cubic, disordered body-centered form (4), and above about 3-kb pressure Bridgman (5) found a cubic form now known to be halite type (6). At 97 kb, Riggleman and Drickamer (7) observed a new phase by means of high-pressure electrical resistance studies; Bassett and Takahashi (8) observed a similar phase change at 110 kb by x-ray and optical methods and proposed that the new phase (V, Fig. 1) has a CsCl-type structure. Bassett and Takahashi also confirmed the existence of another new phase (IV), first found by Van Valkenburg (9), which at room temperature exists in a very narrow stability field near 3 kb.

Phases I, II, and III meet in a triple point at 2.7 kb and 100°C (5). Bassett and Takahashi (8) report another triple point at lower temperature, and at

approximately the same pressure, between phases II, III, and IV.

The pressure interval for the stable existence of the new form (IV) of AgI can be estimated from the photograph in the report by Van Valkenburg [(9) and Fig. 1]. In the photograph the width of the ring Δr pertaining to the new phase is about 0.15 at $r = 0.63$, where r is the fractional radius of the anvil. By considering various types of pressure gradients across the anvil, it appears that the range of pressure for the stable existence of phase IV can be only a few tenths of a kilobar at room temperature.

Van Valkenburg's optical study of this phase showed that it was not isometric. The beryllium vessel technique (10) was considered ideal for the study of the high-pressure x-ray diffraction patterns of this phase. Because of the demonstrated narrow pressure range of stability of the form at room temperature, the sample was packed in cornstarch, and this procedure was highly successful in creating near hydrostatic conditions in the vessel. An estimated 75 percent conversion to the new phase was accomplished with this technique.
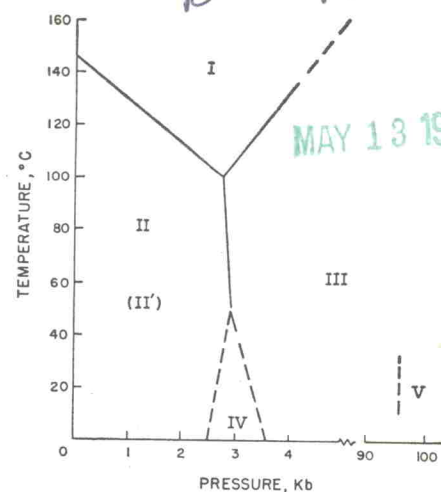

Fig. 1. Phase diagram of silver iodide. The dashed boundaries give the approximate positions of the stability fields of phases IV and V.

However, in all experiments at least one of the two adjacent phases II′ or III was also present, and in most instances, both were present. From this fact, and because heating to 50°C of a mixture of II′, III, and IV at about 3 kb caused the peaks from phase IV to disappear and the peaks from phases

Table 1. X-ray diffraction data for AgI-phase IV at 25°C and 3 ± 0.5 kb.

d_{obs} Å	Hexagonal *		Tetragonal †		Orthorhombic ‡		I/I_0 §
	hkl	d_{calc} Å	hkl	d_{calc} Å	hkl	d_{calc} Å	
6.04	101	6.00	101	6.01	011	6.10	5
3.97	200	3.98	201	3.97	012	4.00	4
3.66	201	3.65	102	3.66	112	3.68	55
2.86	211	2.86	212	2.86	013	2.87	64
2.50	212	2.51	222	2.51	131	2.51	17
2.30	220	2.30	203	2.30	004	2.30	94
2.20	310	2.21	401	2.20	014	2.21	100
					303	2.19	
1.995	400	1.992	004	1.995	140	1.991	40
1.949	401	1.945	104	1.949	141	1.946	40
1.829	320	1.828	204	1.829	142	1.828	20
	223	1.827	500	1.828			
1.624	412	1.622	423	1.621	050	1.630	28
1.503	502	1.503	404	1.503	135	1.504	26
	420	1.506	610	1.503			
			205	1.506			
1.409	503	1.408	612	1.407	434	1.405	16
	206	1.407	541	1.405			
1.380	414	1.377	443	1.381	540	1.380	5
					352	1.379	
1.304	504	1.301	116	1.303	326	1.304	23
	306	1.308	700	1.306	062	1.303	
			613	1.308	260	1.305	
			405	1.308			
1.258	432	1.258	543	1.258	543	1.258	7
	226	1.258	425	1.258	721	1.260	
			444	1.256	262	1.255	
1.246	316	1.243	702	1.241	360	1.246	19
	117	1.241	721	1.240	063	1.243	
					525	1.250	

* $v(H) = 0.1413$ cm³/g ($Z = 12$); † $v(T) = 0.1426$ cm³/g ($Z = 12$); ‡ $v(O) = 0.1518$ cm³/g ($Z = 12$); § Ratios of integrated intensities.

II' and III to increase slightly in intensity, the triple point II-III-IV is probably lower than the 85°C reported by Bassett and Takahashi (8). It is possibly no higher than 50°C and may be even closer to room temperature. The boundaries of phase IV in Fig. 1 are dashed to show only the approximate position of its stability field.

With the use of the beryllium pressure vessel and an x-ray fluid-pressure cell (11), several excellent x-ray diffraction patterns of phase IV have been obtained from which 17 reproducible peaks can be identified. The peaks were first indexed according to a hexagonal cell (H) that appears to be related to the wurtzite-type (II) cell according to the relations

$$a_{II} \cong 2a_{II},$$
$$(h00)_{II} = \tfrac{1}{2}(h00)_{II},$$
$$(hk0)_{II} = \tfrac{1}{2}(hk0)_{II}$$

where $a_{II} = 4.59$ Å, $c_{II} = 7.51$ Å, $a_{II} = 9.20$ Å, and $c_{II} = 9.02$ Å. There does not appear to be any relation between the c-directions of the two structures. Constants for two other cells, tetragonal (T) and orthorhombic (O), can be derived from the hexagonal one according to the relations

$$a_T \cong (a_{II} + c_{II})/2 \qquad a_T = 9.14 \text{ Å}$$
$$c_T = (\sqrt{3}/2)a_{II} \qquad c_T = 7.98 \text{ Å}$$

and

$$a_0 = 1.055\, a_T \qquad a_0 = 9.37 \text{ Å}$$

$$b_0 = 0.892\, a_T \qquad b_0 = 8.15 \text{ Å}$$
$$c_0 = a_{II} \qquad c_0 = 9.20 \text{ Å}$$

Indexing of the three cells can be accomplished with nearly the same degree of fit, and therefore the indices for all three are presented in Table 1. The measured specific volume of phase II at 1 atm is 0.1759 cm³/g, and for phase III at 3 kb, 0.1431 cm³/g. In view of the specific volume of these cells with Z equal to 12 molecules per cell, as presented in Table 1, the orthorhombic cell appears to be the most acceptable. For the tetragonal cell, Z equal to 10 gives a specific volume of 0.1711 cm³/g, a possibility that as yet cannot be ruled out.

It is our suggestion that any further attempt to obtain x-ray diffraction data for this phase should be carried out in an apparatus employing perfectly hydrostatic pressures. We have made several unsuccessful attempts to obtain the phase IV diffraction pattern using the beryllium Bridgman anvil apparatus (12, Fig. 1A). The narrow range of stability of the form combined with the pressure gradient of such devices results in such a small quantity converted [approximately 15 percent in the anvil shown in Fig. 1 of the Van Valkenburg paper (9)] that it is difficult to obtain definitive x-ray diffraction patterns. It is evident, however, that pressure gradients in the anvil device can be considerably reduced by cycling the pressure up and down until there is no more extrusion of the sample (9, p. 97).

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