

High-Pressure Melting and Phase Transitions in Silver Halides

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NO previous investigation of the effect of high pressure on the melting points of silver halides has been reported. Since silver chloride is widely employed as a solid pressure container, often at high temperatures,¹ a determination of the pressure dependence of its melting is of special importance. Completion of the high-pressure phase diagram of silver iodide, first studied by Tammann² and Bridgman,³ is also of considerable interest. In the present study, the effect of pressures to 57 kilobars (kbar) on the melting points of AgCl, AgBr, and AgI has been measured using a differential thermal conductivity technique. The solid-solid transition boundaries in silver iodide at low pressures have also been roughly determined. The melting curves have been analyzed by determining if they can be fit with the Simon equation and by comparing their initial slopes with those calculated using the Clapeyron equation.

The experimental techniques utilized in the present work have been described in detail earlier^{4,5} and will not be discussed in length here. The experiments were performed in a tetrahedral anvil device, the phase transitions being monitored by differential thermal conductivity analysis. Chromel-Alumel thermocouples were used for temperature measurement, and no correction was made for the effect of pressure on their output. Temperatures are thought to be accurate to $\pm 1.5\%$. Room-temperature pressure calibration carried out in the usual manner was utilized.⁶ Pressures are believed accurate to $\pm 2.5\%$ above 20 kbar and ± 0.5 kbar below 20 kbar. All data were recorded automatically on X-Y recorders. The sources and purities of the materials used were as follows: (1) the silver chloride was from Baker Chemical Company, stated to be 99.7% pure; (2) the silver bromide was from Fisher Scientific Company, stated to be purified; (3) the silver

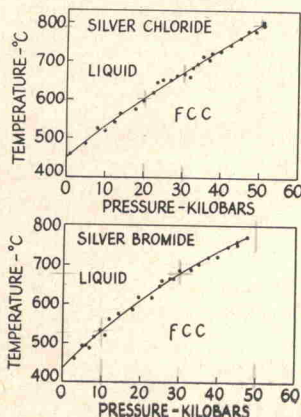


FIG. 1. Melting curves of silver chloride and silver bromide. The solid curves represent the Simon equation using parameters from Table I.

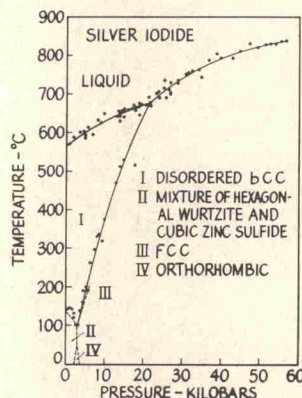


FIG. 2. Pressure-temperature phase diagram of silver iodide. The solid curves through the experimental melting points represent the Simon equation using parameters from Table I.

iodide was from Fisher Scientific Company and stated to be chemically pure.

At room temperature and atmospheric pressure, AgCl and AgBr crystallize in the face-centered cubic (fcc) sodium chloride structure, whereas AgI crystallizes in either the cubic zinc sulfide structure or the hexagonal wurtzite structure.⁷ Phase transitions in AgCl and AgBr at about 90 and 85 kbar, respectively, have been reported and tentatively supposed to be transformations from sodium chloride to the cesium chloride type structure.^{8,9} Application of approximately 3-kbar pressure causes silver iodide to transform to the fcc lattice.¹⁰ Above 145°C, at atmospheric pressure, silver iodide exists in a body-centered cubic (bcc) lattice in which the iodide ions are at the points of the bcc lattice and the silver ions are disordered.¹¹ Very recent work¹²⁻¹⁴ has shown that silver iodide transforms to the cesium chloride structure above 110 kbar^{14a} and, in addition, exists in yet another crystallographic modification near 3 kbar. The crystal structure of this newly discovered phase is still somewhat uncertain but is probably orthorhombic.¹³

The results of the present study on the melting of AgCl and AgBr are shown in Fig. 1. No polymorphic transitions were observed in the pressure-temperature range of this work, and no indications of irregularity are seen in the melting curves. The silver chloride melting curve has an initial slope of 8°C/kbar and shows a slight concavity toward the pressure axis. The silver bromide melting curve is also slightly concave toward the pressure axis and has an initial slope of 10°C/kbar. Each of the curves is seen to extrapolate quite well to the accepted atmospheric pressure melting points, 455°C for AgCl and 434°C for AgBr.

The present data on the pressure-temperature phase diagram of silver iodide are shown in Fig. 2. The dashed lines are the data of

TABLE I. Comparison of experimental and calculated initial slopes.

Compound	T_0 (°K)	c	a (kbar)	Clapeyron $\frac{dT_m}{dP_m} \left(\frac{^\circ\text{K}}{\text{kbar}} \right)$	Experimental $\frac{dT_m}{dP_m} \left(\frac{^\circ\text{K}}{\text{kbar}} \right)$
AgCl	728	1.7	55.0	13 ^a	8
AgBr	707	2.5	28.0	18 ^a	10
AgI (I)	830	8.5	9.5	14 ^a	10
AgI (III)	953 (at 22 kbar)	8.5	12.5	...	9

^a Latent heats from L. Brewer, Natl. Nuclear Energy Ser. Div. IV, **19B**, 204 (1950). Volume changes from H. Schinke and F. Sauerwald, *Z. Anorg. Allgem. Chem.* **287**, 313 (1956) for AgCl and AgBr; and G. F. Rodwell, *Phil. Trans.* **173**, 1125 (1883) for AgI.

Bridgman³ except in the case of AgI (iv) where the approximate data of Davis and Adams¹³ are shown. In the present work the phase boundaries between the solid polymorphs AgI (II) and AgI (I), AgI (I) and AgI (III), and the melting curve have been determined. No data were obtained on the transitions below 100°C at very low pressures because of equipment limitations. The data agree fairly well with Bridgman except in the case of the II-I transition. The I-III transition line joins the melting curve at a triple point at about 22 kbar and 680°C. The initial slope of the silver iodide melting curve is 10°C/kbar and the melting curve extrapolates to an atmospheric melting point of 563°C whereas the accepted value is 557°C.

Knowledge of the change of volume and latent heat upon melting at atmospheric pressure permits calculation of the initial slope of the melting curve from Clapeyron's equation

$$dT_m/dP_m = \Delta V/\Delta S, \quad (1)$$

where T_m and P_m are the temperature and pressure at the melting point, and ΔV and ΔS are the changes of volume and entropy on melting. Table I gives, for the silver halides, a comparison of the experimental initial slopes and the initial slopes calculated using the Clapeyron equation in conjunction with experimental values of ΔV and ΔS of indicated source. The agreement between the two slopes is not good, the observed slopes being about 50% lower than those calculated from Eq. (1). Similar disagreement was found by Clark¹⁵ in the case of eight alkali halides. It appears, as Clark suggested, that the experimental values of ΔV have been overestimated, or the values of ΔS consistently underestimated.

The silver halide melting curves, as determined in the present study, can be represented quite well by the Simon equation

$$P_m - P_0 = a[(T_m/T_0)^c - 1], \quad (2)$$

where P_m and T_m are the pressure and absolute temperature at the melting point, T_0 is the melting point at pressure P_0 , and a and c are adjustable constants. The quantity P_0 differs from zero only for the melting of AgI (III), P_0 and T_0 in this case being the coordinates of the triple point at 22 kbar and 680°C. The experimental melting points were fit to Eq. (2) by using an approximation procedure similar to that of Clark.¹⁵ The parameters of the Simon equation obtained are given in Table I; the solid lines in the figures represent the Simon equation using these values of a

and c . In the process of obtaining the best fit to the experimental points, the uncertainties in the values of a and c given in Table I were estimated to be about $\pm 3\%$. It is seen that the values of a and c for both phases of AgI are considerably different from those of AgCl and AgBr.

Considerable effort has been expended in fitting high pressure melting curves to the Simon equation.¹⁶ In addition, many theoretical attempts at the derivation of this equation and the physical interpretation of its variable parameters have been made.¹⁷⁻¹⁹ At the present time no completely satisfactory theoretical explanation of the Simon parameters exists but it is probable that the quantity a is related to the internal pressure while c is related to the interatomic potential energy function and the dynamics of the lattice through the Gruneisen parameter.¹⁷⁻¹⁹

The large differences observed in the Simon parameters of AgCl and AgBr on the one hand and the two phases of AgI on the other are somewhat surprising. Two possible explanations of these differences in Simon parameters may be considered: (1) the presence of the triple point in AgI near 22 kbar would tend to depress the melting point curve, causing a discrepancy in the Simon parameters, and (2) a fundamental difference might exist in the interatomic bonding of AgI as compared with AgCl and AgBr. The former explanation might very well account for the observed differences, especially in the Simon parameters of AgI (I). The latter explanation given above is based on a theoretical calculation of the lattice energies of the silver halides by Mayer.²⁰ This study showed that AgCl and AgBr can be considered to be very nearly entirely ionic, whereas AgI exhibits approximately 10% homopolar bonding. This fundamental difference in interatomic bonding could give rise to the observed difference in Simon parameters, particularly if these parameters are actually related to the interatomic potential.

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^{14a} It should be pointed out that the exact pressures of the transitions in the silver halides near 100 kbar are somewhat uncertain because of the difficulty of pressure calibration in this pressure range. For example, B. M. Riggleman and H. G. Drickamer [*J. Chem. Phys.* **38**, 2721 (1963)] reported a resistance transition in silver iodide at 97 kbar; this presumably is the same transition as that reported at 110 kbar in Ref. 12. There also exists recent evidence that the silver chloride transition may occur at a pressure considerably lower than 90 kbar (P. W. Montgomery, paper presented at ASME Meeting, New York, December 1964).

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