

Pressure-Induced Trapping Phenomenon in Silver Iodide

Abstract. Observations of the optical properties and electrical conductivity of silver iodide at pressures between 2 and 4 kilobars are indicative of the formation of free silver (or silver and iodine) in this pressure range. On the basis of the sequence of events and the volume relations, this reaction could account for the smooth and reversible phase transformations of silver iodide in this pressure range. The phenomenon may be due to the trapping of an electron by the silver ion (in a thermally excited state) as a result of the distortion of the lattice under pressure.

Observations of silver iodide under pressure in a diamond anvil high-pressure cell have led us to the conclusion that the compound is unstable with respect to silver, and perhaps iodine, near the transformation pressure, reported by Bridgman to be 3.0 kb (1). The following experiments provide evidence to support this view:

1) The shift of the absorption edge of silver iodide with pressure observed in this laboratory differs slightly from that reported by Slykhouse and Drickamer (2) in that the absorption edge near the transformation shifts from 22,000 cm^{-1} all the way through the visible and infrared regions (to a value less than 650 cm^{-1}); this difference suggests the presence of metallic silver.

2) When silver iodide is observed in the diamond cell at an applied pressure of 3 kb, a diffuse black band separates the atmospheric phase from the high pressure (NaCl) phase found by Bridgman. The broadness of this band is time-dependent so that within a few hours a very narrow band or line results (Fig. 1) as the silver iodide in the region of the original band comes to equilibrium to form the intermediate phase of silver iodide found by Van Valkenburg (3). If the pressure on the silver iodide is diminished very slowly, the black line remains in the low pressure phase (Fig. 2). The procedure can be repeated by further pressure reductions to give further lines. These lines slowly disappear over a period of 1 to 2 hours in the low pressure phase.

3) A similar darkening is observed in silver iodide at considerably higher pressures, that is, near 40 to 60 kb. This darkening occurs rather slowly, re-

quiring several hours to become a very dark brown color. If the pressure on this darkened area is diminished rapidly, the small black specks disappear rapidly, leaving a reddish stain suggestive of free iodine. The stain disappears over a period of 16 hours in the high pressure phase at 5 kb. If the pressure on the sample is reduced to 1 atm, the reddish stain remains for a time, disappearing in 10 to 15 minutes. The stain can be removed in a few seconds by increasing and decreasing the pressure in a manner which sweeps the dark band (of silver) back and forth through the stained area.

4) The electrical conductivity of the silver iodide at room temperature increases several hundred times in the region of the darkened band. These experiments were conducted in the diamond anvil high-pressure cell and were necessarily subject to a relatively large error. The conductivity of the silver iodide at atmospheric pressure was measured to be $5 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$, while the material in the region of the black band had a conductivity of $1.9 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$. Baranovskij *et al.* (4) report such a 500-fold increase in conductivity in the 3 to 4 kb range. The lack of experimental details and values make a comparison difficult although the observation appears to be of the same phenomenon. They explain the anomaly on the basis of "additional lattice defects formed at the phase boundary and near dislocation regions."

A list of those forms believed to exist over a range of pressures is shown in Table 1. These observations do not appear to be inconsistent with the present studies or the predictions of Huggins (5).

One concern in the study of pressure-induced phase transformations is the origin of the transformation, that is, the particular event which triggers the transformation. We are particularly concerned with transformations which occur smoothly and reversibly at room temperature, such as the transformations in silver iodide, for it seems reasonable that some phenomenon other than the mere compression of molecules must be responsible for such smooth and reversible transformations. The mechanism might well be initiated by a chemical or electronic phenomenon occurring within the molecules composing the crystal. Such reactions could initiate the phase transformation in much the same manner that ther-

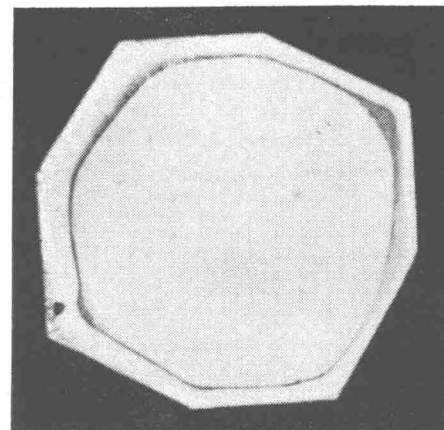


Fig. 1. Silver iodide in diamond anvil high-pressure cell at an applied pressure of 4 kb ($\times 100$).

mal excitation initiates temperature-induced transformations. Since free silver (or silver and iodine) appears to be formed in the range of 2 to 4 kb and particularly since this is the first observable event (consistently preceding the phase transformations), we propose that the phase transformations in this pressure range are initiated by the formation of free silver.

Some attention should be given to the volume changes accompanying the formation of silver and iodine from silver iodide. At 3 kb, the molecular volume of silver iodide is 40.90 $\text{cm}^3 \text{ mole}^{-1}$, while the volumes of free silver and iodine at this pressure are 10.24 $\text{cm}^3 \text{ g-atom}^{-1}$ and 25.59 $\text{cm}^3 \text{ mole}^{-1}$, respectively. The total, 35.83 $\text{cm}^3 \text{ mole}^{-1}$, is larger than the volumes of a proposed orthorhombic phase (6) (35.64 $\text{cm}^3 \text{ mole}^{-1}$) and the NaCl phase at 3 kb (35.28 $\text{cm}^3 \text{ mole}^{-1}$). These volume relations are thermodynamically consistent and give further support to the

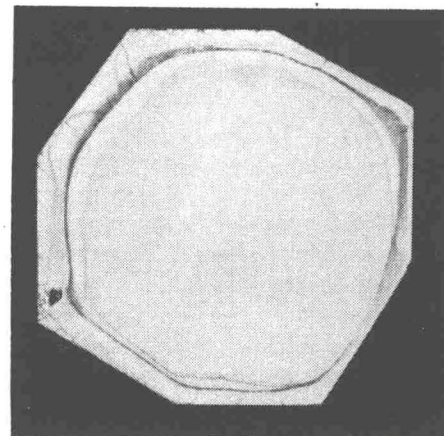


Fig. 2. Sample in Fig. 1 with pressure reduced to 3 kb.

Table 1. Crystalline phases of silver iodide at 25°C.

| Pressure (kb) | Crystalline forms | Ref. |
|---------------|------------------------------------|-------|
| Up to 0.1 | Predominantly hexagonal (wurtzite) | 8 |
| 0.1 to 2.4 | Cubic (zinc blende) | 8 |
| 2.4 to 2.9 | Hexagonal or orthorhombic(?) | 6, 9 |
| 3.0 to 97 | Cubic (NaCl) | 10 |
| Above 97 | Cubic (CsCl)(?) | 5, 11 |

orthorhombic assignment of Davis and Adams.

Silver iodide has an absorption band at 23,600 cm^{-1} which results in a sharper absorption edge than that observed in the other silver halides. Seitz has attributed this peak to a $d^{10} \rightarrow d^9s$ transition in the Ag^+ ion (7). This transition is said to be forbidden in the free silver ion but becomes allowed (in silver iodide) because of the tetrahedral coordination of the silver ion site. The low cubic and hexagonal forms of silver iodide have such

tetrahedral coordination, whereas the NaCl structure has octahedral coordination. Slykhouse and Drickamer have shown that this absorption band virtually disappears in the range of the phase transformations (near 3 kb) as expected from Seitz's hypothesis (2).

The formation of free silver might therefore be due to a trapping of an electron by the thermally excited d^9s silver ion since the transition becomes unallowed as the tetrahedral symmetry is disturbed by the compression of the low cubic form of silver iodide. The intermediate phase which forms slowly is then expected to be a phase in which the tetrahedral symmetry is less disturbed by pressure.

Observations of the cuprous halides and cadmium sulfide under pressure indicate that a similar series of events takes place in these compounds at pressures in the vicinity of the lowest pressure transformations. For example, the separation of free copper into a bronze colored film has been observed in

cuprous bromide. However, the thermodynamics and kinetics of these reactions appear to be such that each material will have to be investigated independently.

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