

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.

H. C. DUECKER

National Bureau of Standards,
Washington, D. C.

ELLIS R. LIPPINCOTT

University of Maryland, College Park

References

1. P. W. Bridgman, *Proc. Am. Acad. Arts Sci.* **51**, 53 (1915).
2. T. E. Slykhouse and H. G. Drickamer, *J. Phys. Chem. Solids* **7**, 207 (1958).
3. A. Van Valkenburg, *J. Res. Natl. Bur. Stds.* **68A**, 97 (1964).
4. V. I. Baranovskii, B. G. Lurie, A. N. Murin, *Dokl. Akad. Nauk SSSR* **105**, 1188 (1955).
5. M. L. Huggins, in *Phase Transformations in Solids*, R. Smoluchowski, Ed. (Wiley, New York, 1951), pp. 238-56.
6. B. L. Davis and L. H. Adams, *Science* **146**, 519 (1964).
7. F. Seitz, *Rev. Modern Phys.* **23**, 328 (1951).
8. G. Burley, *Am. Mineral.* **48**, 1266 (1963).
9. W. A. Bassett, personal communication.
10. R. B. Jacobs, *Phys. Rev.* **54**, 325 (1938).
11. B. M. Riggelman and H. G. Drickamer, *J. Chem Phys.* **38**, 2721 (1963).

13 October 1964