THE AMERICAN MINERALOGIST, VOL. 50, OCTOBER, 1965

SILVER IODIDE POLYMORPHS

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ABSTRACT

Stability fields, and crystal structures of six polymorphs of silver iodide have been investigated by optical and *x*-ray techniques employing a high pressure diamond cell up to 200° C. and above 100 kilobars. Two triple points have been fixed; one at 98±2° C. and 3.1±0.4 kilobars and the other at 65±2° C. and 3.1±0.4 kilobars. The former is in close agreement with previous determinations by Bridgman; the latter has not been previously reported. A high pressure phase transformation has been measured at 100±5 kilobars. The *x*-ray diffraction pattern of the phase above 100 kilobars cannot be indexed as cubic, suggesting the formation of asymmetric covalent bonding, which is consistent with other lines of evidence.

INTRODUCTION

Studies of atomic arrangements and stabilities of polymorphic forms of elements and compounds as a function of pressure and temperature contribute to our fundamental understanding of the nature of bonding and of phase transformations in crystalline solids. Silver iodide is of particular interest since 1) as many as six polymorphic phases are known, 2) the atomic arrangements in some of these phases are common to many other binary compounds, and 3) substantial information has recently become available for a wide range of pressures and temperatures.

The purpose of this paper is to present new *x*-ray diffraction and optical data on silver iodide, to delineate stability fields of some of its polymorphs as a function of pressure and temperature and to discuss the changes in atomic arrangements and the nature of bonding, particularly with increasing pressure. Most of the new data presented here were obtained by microscopic, spectrophotometric, and *x*-ray diffraction methods applied to polycrystalline specimens compressed in a diamond anvil cell.

In succeeding discussions in this paper the phases for which crystal structures are known are designated by the crystal structure names and those whose crystal structures are not known are named for the lowest pressure at which they are stable at room temperature. Designations used by other workers are given in Table 1.

PREVIOUS WORK

Silver iodide specimens prepared by a variety of methods at room temperature and one atmosphere pressure have been found to consist commonly of a mixture of two phases: one having a *sphalerite-type* structure and the other having a *wurtzite-type* structure. Majumdar and Roy

TABLE 1. DESIGNATIONS OF SILVER IODIDE POLYMORPHS

This report	Roman numerals	Greek letters	Strukturbericht
Wurtzite	II	beta	B4
Sphalerite	(II′)	gamma	B3
Body-centered cubic	I	alpha	B23
3 kilobar	IV	—	—
Rock salt	III	—	B1
100 kilobar	V	—	—

(1959) conducted a systematic study of these two phases by preparing silver iodide by a number of different methods. Out of eleven methods they found that eight produced a mixture of the two phases, and three yielded the *wurtzite* phase alone. Heating of the mixtures resulted in conversion of the *sphalerite* to the *wurtzite* phase. They, therefore, concluded that the *wurtzite* phase is thermodynamically stable and the *sphalerite* phase is metastable at one atmosphere pressure and below 147° C. Burley (1963) arrived at a similar conclusion from prolonged heating of samples just below 147° C. He pointed out, however, that compressing a mixture of these phases in a die or grinding it in a mortar and pestle converts it to the *sphalerite* phase. However, his investigation did not resolve the question of the stability of the *sphalerite* phase under pressure.

At one atmosphere pressure between 147° C. and 558° C. a high temperature phase becomes stable. The structure of this phase has been described by Strock (1934) as consisting of the anions in a body-centered cubic arrangement with the cations randomly distributed interstitially among the anions. The electrical conductivity of silver iodide as a function of temperature has been measured by Turbant and Lorenz (1914) as a function of temperature and by Lieser as a function of temperature and pressure. They found that silver iodide is essentially an insulator up to 147° C. and up to 150 bars. On the other hand, it has a high conductivity above 147° C. which has been attributed to the high mobility of the silver ions among the iodine ions (Huggins, 1951; Lieser, 1958).

Bridgman (1915) studied the compressibility of silver iodide up to 12 kilobars and 200° C. and discovered a volume discontinuity at 2.96 kilobars at 30° C. He proposed a triple point at 2.76 kilobars and 99.4° C., where the I (*body-centered cubic*), II (*wurtzite-sphalerite*), III (*rock salt*) phases coexist (Fig. 1). The crystal structure of the high pressure phase was determined by Jacobs (1938a) to be a *rock salt* structure by means of x-ray diffraction under pressure. More recently, this determination has been confirmed by Piermarini and Weir (1962).

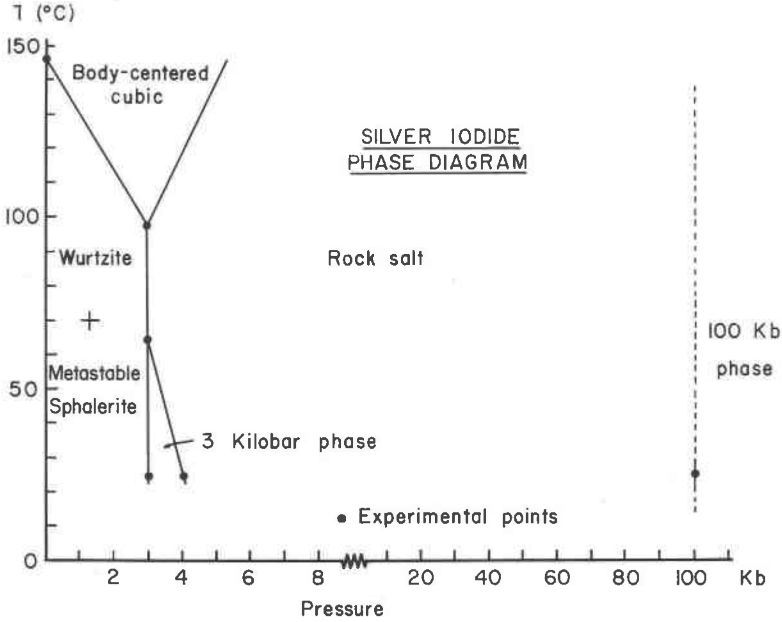

FIG. 1. The phase diagram for silver iodide. The dashed line indicates an uncertain boundary.

The polarizing microscope was used by Van Valkenburg (1964) to study silver iodide compressed between two diamond anvils. He observed a new, strongly birefringent polymorph at approximately 3 kilobars, separating the *wurtzite* and *rock salt* phases. Duecker and Lippincott (1964) found that silver iodide becomes strongly absorbing to visible light at 3 kilobars on initial compression and have suggested that this is due to electron trapping by silver ions. Davis and Adams (1964) obtained an *x*-ray diffraction pattern of a polycrystalline specimen which was held at a hydrostatic pressure of approximately 3 kilobars in a beryllium die. They found that they could index their pattern as hexagonal, tetragonal, or orthorhombic but favored orthorhombic since its specific volume falls between those of the *wurtzite* and *rock salt* phases, if a unit cell is assumed to contain twelve molecules.

Slykhouse and Drickamer (1958) have investigated the effect of pressure on the absorption edge of silver iodide in visible light and Riggleman and Drickamer (1963) studied the effect of pressure on the electrical resistance. They found a high pressure phase stable above 97 kilobars at room temperature (Fig. 1). The same high pressure phase has been reported by Van Valkenburg (1964) to be birefringent and have higher refractive indices than the *rock salt* phase.

INSTRUMENTATION

The instrument used in the present study has been modified from a high pressure cell developed by Van Valkenburg (1963) which employs two diamond anvils of gem quality. The modifications were made to permit both *x*-ray diffraction studies and optical observations of a sample under pressure. Optical examinations make it possible to select a particular phase or area of a specimen for study by *x*-ray diffraction. In addition, an electric resistance heater has been added for high temperature studies up to 300° C.

The sample in polycrystalline form is placed between the polished faces (0.5 mm. diameter) of two diamonds mounted on the ends of pistons which are guided by a cylindrical sleeve (Fig. 2). This sleeve may be replaced by a ceramic cylinder which contains a resistance heater for high temperature studies. The pistons are driven together by a lever, screw, and spring assembly. A hole in one of the pistons permits a finely collimated (0.05 mm. diameter) *x*-ray beam of monochromatized Mo Kα radiation to pass through one of the diamonds and impinge on the sample. The collimator is a glass capillary tube which passes enough light to per-

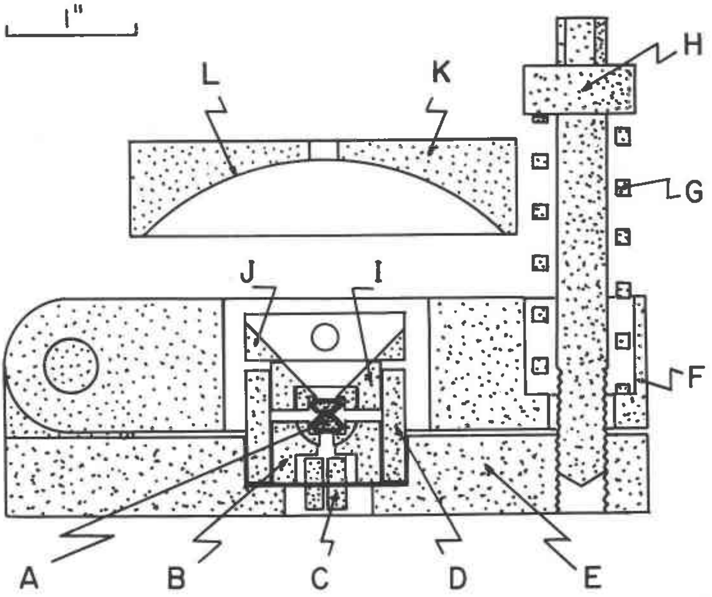

FIG. 2. Diamond anvil high pressure cell. A) Diamond anvils, B) lower piston, C) colimator, D) sleeve, E) lower jaw, F) upper jaw, G) spring, H) screw, I) upper piston, J) gimbal, K) film cassette, and L) film.

mit visual observations for alignment purposes. The collimator, however, must be removed for studies with polarized and monochromatic light. X-rays diffracted by the sample pass through the other diamond, out through a conical hole in the other piston and are then recorded photographically on a cylindrical film with a 50 mm radius.

Optical observation of the sample can be made with a petrographic microscope by passing light through the diamonds. As the diamonds are driven together sample extrudes from between the faces until friction prevents further extrusion. As a result a pressure gradient exists from a maximum at the center of the sample area to essentially 1 bar at the periphery. As force is applied a high pressure phase appears at the center of the sample area and spreads outward. This pressure gradient permits the observation of several phases simultaneously (Figs. 3–7). Different phases are usually distinguishable by differences in refractive index and often by differences in color.

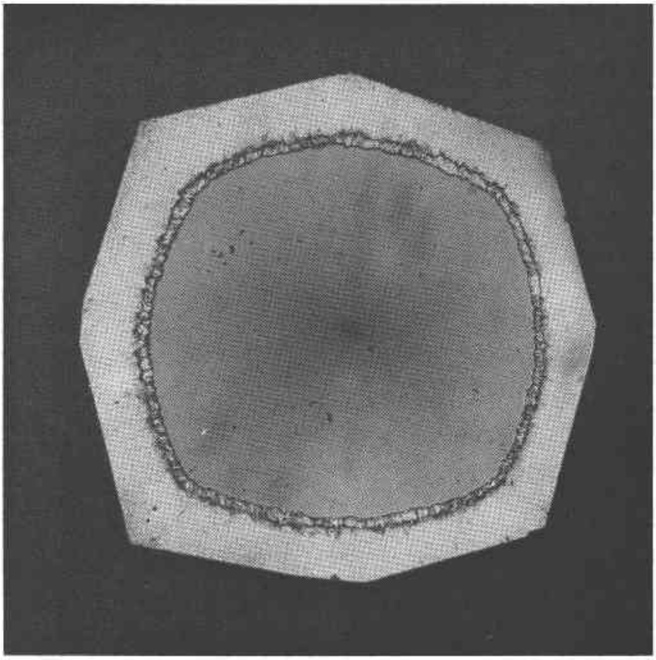

FIG. 3. Photomicrograph of silver iodide under pressure as viewed through the upper diamond. The pressure at the center of the sample area is approximately 15 kilobars and grades to 1 bar at the periphery. The central area has the *rock salt* structure, the thin ring is the *3 kilobar* phase and the surrounding area has the *sphalerite* structure. The diameter of the octagonal area is 0.5 millimeter.

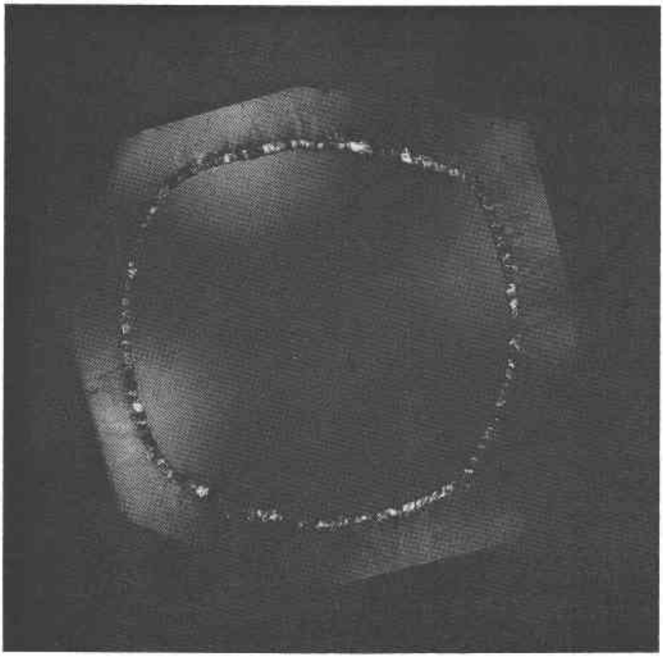

FIG. 4. The same as Fig. 3 between crossed polars. The dark cross results from strain on the diamond anvils. The *3 kilobar* phase shows strong birefringence.

X-ray diffraction patterns can be made of any phase by adjusting the pressure so that the phase appears in the center of the sample area where the *x*-ray beam passes through.

THE POLYMORPHS OF SILVER IODIDE

Wurtzite and Sphalerite Phases. Investigations of previous workers such as Majumdar and Roy (1959) and Burley (1963) have led to the conclusion that the *wurtzite* is the thermodynamically stable phase below 147° C at one atmosphere pressure. On the other hand, it has been reported (Burley, 1963) that the *wurtzite* phase may be readily and reproducibly converted to the *sphalerite* phase when ground by mortar and pestle or compressed to a pellet in a die under pressures over 100 bars. Such observations pose a question concerning the possible existence of a stability field for the *sphalerite* phase at high pressures. Visual observations in the diamond anvil cell make it possible to study the stability of the *sphalerite* phase under various pressure-temperature conditions.

In a polycrystalline specimen consisting of a mixture of the *wurtzite* and *sphalerite* phases, the *wurtzite* phase occurs as birefringent needles (Fig. 8). If such a mixture is compressed so that no extrusion takes place,

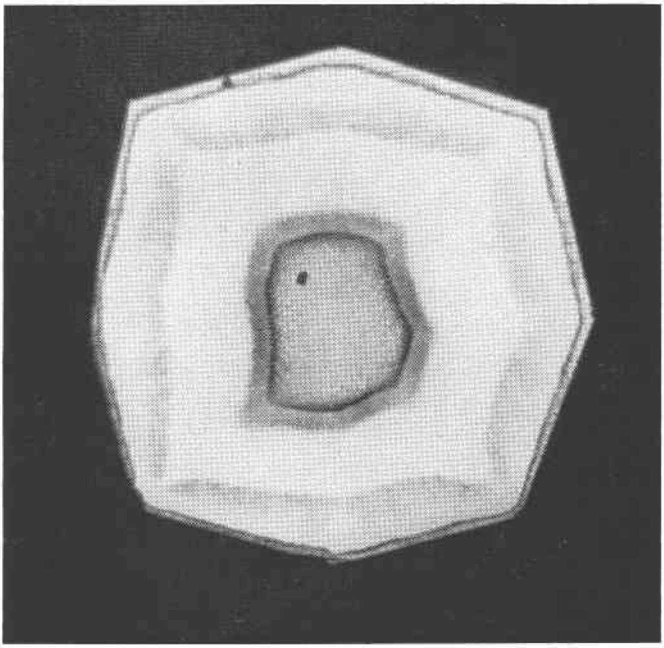

FIG. 5. Photomicrograph of silver iodide with a central pressure of 100 kilobars. Darkened areas may be seen at approximately 40 and 70–100 kilobars in the *rock salt* phase. The phases seen in Figs. 3 and 4 are crowded toward the periphery in this photograph.

wurtzite needles persist up to the 3 kilobar phase boundary. However, if extrusion takes place, the *wurtzite* needles are destroyed and the sample becomes nearly isotropic. An x-ray diffraction pattern of this material indicates that it is predominantly the *sphalerite* phase. Thus, strong shearing accompanying extrusion appears to favor the formation of the *sphalerite* phase in preference to the *wurtzite* phase. Grinding in a mortar and pestle and compaction in a die almost certainly produce shear which may be responsible for the formation of the *sphalerite* phase reported by others. Birefringent needles of the *wurtzite* phase reappear when the *sphalerite* phase is heated above 55° C. at pressures below the 3 kilobar phase transformation. Higher temperatures favor the formation of the *wurtzite* phase which persists indefinitely when cooled to room temperature. The boundaries separating the two phases are sharp indicating that the *wurtzite* phase is a discrete, non-cubic rather than distorted cubic phase.

Therefore, *wurtzite* probably is the thermodynamically stable phase over the temperature pressure range in which both can be found. *Sphalerite* is probably metastable and may have no stability field. This conclusion is consistent with those of Majamdar and Roy (1959) and Burley

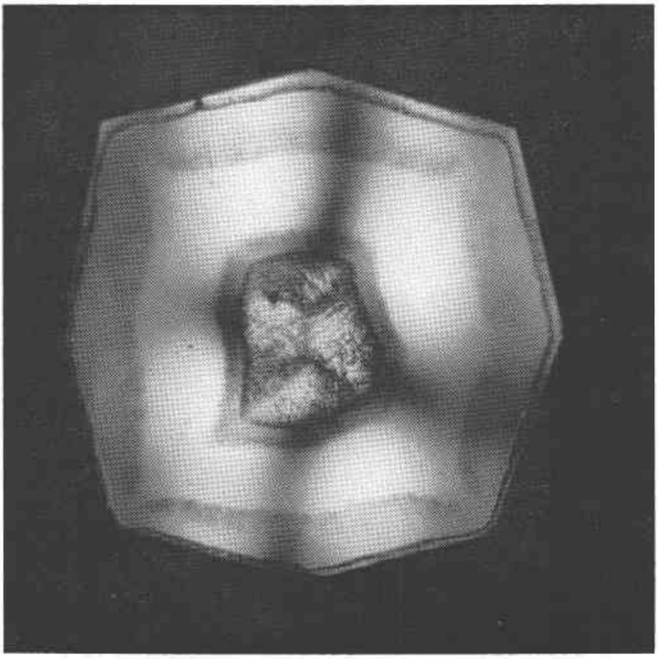

FIG. 6. The same as Fig. 5 between crossed polars. The *100 kilobar* phase appears as a fine grained birefringent area. The greater strain causes the diamonds to be more anisotropic than Figure 4.

(1963, 1964). The ease with which silver iodide can pass from one of these phases to the other over a range of pressure-temperature conditions suggests that the free energy difference between the two is very small over that range and may be easily influenced by the free energies originating in lattice defects and surface conditions.

Body-centered Cubic Phase. The *body-centered cubic* phase appears as a lemon yellow area at temperatures above 147° C. when no pressure is applied and at 98° C. where the sample is at approximately 3 kilobars. It appears as a ring separating the *wurtzite* and *rock salt* phases at temperatures between 98° C. and 147° C. (Fig. 7). The stability field of this phase has been well established by Bridgman (1915) (Fig. 1).

3 Kilobar Phase. This phase occurs between approximately 3 and 4 kilobars as a thin ring (Fig. 3). It is characterized by 1) a high birefringence (Fig. 4) ,2) a darker yellow color than the phases at pressures just above and below due to a sharp absorption edge at 4760 Å, 3) refractive indices which are higher than those of the *sphalerite* and *wurtzite* phases and lower than the *rock salt* phase, and 4) a complex x-ray powder diffraction pattern which cannot be uniquely indexed. The diffraction patterns obtained in the course of this investigation agree with the data reported by Davis and Adams (1964). However, identification of the structure has not been possible.

Optical and x-ray observations reveal that during a period of approximately an hour after compression, the *3 kilobar* phase becomes coarsely crystalline with well defined single crystal domains (Figs. 3 and 4). The coarsely crystalline nature of the phase causes the x-ray diffraction patterns to be spotty.

The *3 kilobar* phase exhibits an unusual relationship with the low pressure phases. When a mixture of *wurtzite* and *sphalerite* phases is compressed above 3 kilobars, both are transformed into the *3 kilobar* phase. However, with decreasing pressure, it transforms into the *sphalerite* but not the *wurtzite* phase. Under the microscope the outline of a domain of the *3 kilobar* phase may be seen after being converted back to the *sphalerite* phase by lowering the pressure. When the pressure on a portion of the sample is repeatedly raised and lowered across the *3 kilobar* transforma-

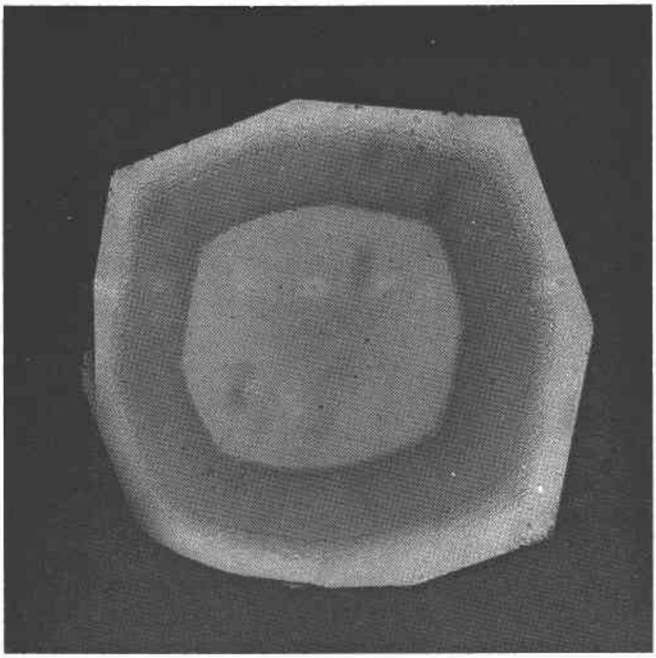

FIG. 7. Photomicrograph of silver iodide with a central pressure of approximately 15 kilobars and a temperature of approximately 120° C. The central phase is *rock salt*, the ring is *body-centered cubic*, and the outer portion is *wurtzite* plus *sphalerite*.

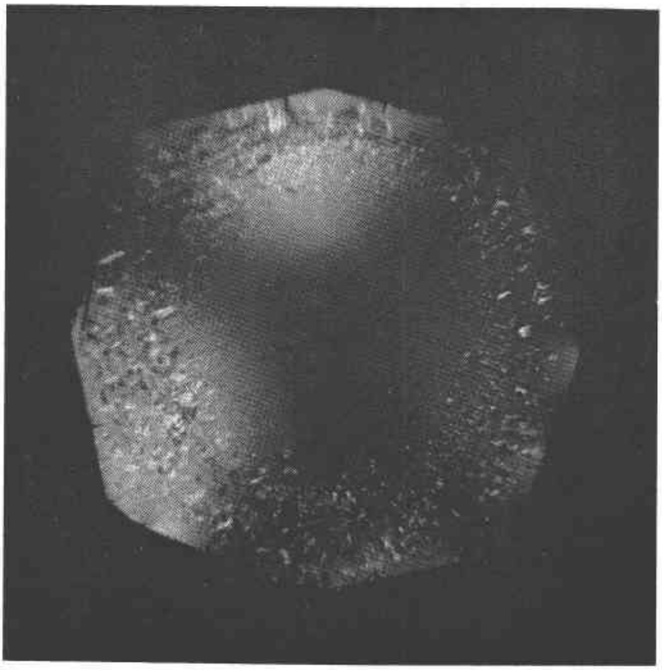

FIG. 8. Photomicrograph of silver iodide between crossed polars. Central pressure is 3 kilobars and the temperature has been raised to 120° C. and lowered to 25° C. A mixture of *wurtzite* (birefringent needles) and *sphalerite* (isotropic matrix) phases results from this treatment.

tion, single crystal domains of the *3 kilobar* phase always reappear in the same places. This indicates that the *sphalerite* phase has a "memory" for the single crystal domains of the *3 kilobar* phase. This behavior suggests that the transformation between the *3 kilobar* phase and the *wurtzite* and *sphalerite* phases is displacive rather than reconstructive. On the other hand, there is no such "memory" relationship between the *3 kilobar* and *rock salt* phases. This implies that this transformation is reconstructive.

The pressures of the upper and lower phase boundaries of the *3 kilobar* phase at 25° C. have been estimated by visual comparisons of the boundaries with a known phase transformation. For this purpose rubidium chloride was selected since it has a distinct phase transformation at 5.3 ± 0.4 kilobars at 25° C. (Pistorius, 1964). Figure 9 shows silver iodide and rubidium choride samples placed side by side in the diamond anvil press. The pressures in the silver iodide may be estimated by assuming 1) the pressure at the edge of the diamond cell is 1 bar, 2) the pressure distribution within the rubidium chloride and silver iodide is the same, 3) the pressure gradient is linear in the region of the phase boundaries, and

4) the optical discontinuity in the rubidium chloride represents the 5.3 kilobar phase transformation. The second asssumption is yet to be substantiated; the third has been demonstrated by Lippincott and Duecker (1964) for substances that go through no phase transformation. Where there is a phase transformation, substances as plastic as rubidium chloride and silver iodide probably have nearly linear gradients. The first and fourth are generally accepted. By this technique the upper and lower boundaries of the *3 kilobar* phase have been estimated to be 4.0±0.4 kilobars and 3.1±0.4 kilobars at 25° C. respectively.

Bridgman (1915) reported that silver iodide exhibits a sharp phase transformation from phase II (*wurtzite* and *sphalerite*) to phase III (*rock salt*) at 2.96 kilobars and 30° C. with a region of indifference of 0.06 kilobars. It is quite unlikely that his instrument lacked the resolution necessary to detect the *3 kilobar* phase. There are two possible explanations for his missing it: 1) the volume difference across one of the phase boundaries may be too small for him to have detected, or 2) the sample may not have had the necessary time for the *3 kilobar* phase to form.

Rock Salt Phase. This phase, stable between 4 and 100 kilobars at room temperature, ranges in color from yellow at 4 kilobars to reddish-brown at 100 kilobars. This change in color is due to a shift in the absorption edge from about 5200 Å to about 6700 Å (Slykhouse and Drickamer, 1958).

At pressures between approximately 70 to 100 kilobars the *rock salt* phase becomes very dark over a period of several hours especially when exposed to an intense light source. Absorption by this darkened area takes place over the whole visible spectrum. In the sample shown in Fig. 5 the darkening can be seen as a ring close to the 100 kilobar boundary. When pressure is decreased, the darkened area remains as a reddish stain which fades over a period of hours if preserved as the *rock salt* structure or in a few minutes if the pressure is completely released. Riggleman and Drickamer (1963) reported greater electrical conductivity between 70 and 100 kilobars than would be expected from their optical absorption measurements. These observations are similar to those made by Duecker and Lippincott (1964) who found that the darkened sample at about 3 kilobars absorbs in the visible and infrared and measured an electrical conductivity which is 380 times as great as the conductivity of silver iodide at room temperature and 1 bar pressure. They conclude that the darkening may be due to electron trapping by silver ions to produce metallic silver. A similar process may be taking place at the higher pressures.

A similar darkening also occurs at approximately 40 kilobars in the *rock salt* phase (Fig. 5). It too seems to be light sensitive but does not become as dark as the 3 and 70–100 kilobar regions. Details of the mechanisms involved are not understood.

100 Kilobar Phase. At 100 ± 5 kilobars silver iodide goes through another phase transformation to a phase which has a higher refractive index and is birefringent (Figs. 5 and 6). The pressure of this transformation was calculated from the unit cell dimensions of sodium chloride mixed with the silver iodide and is in good agreement with the value of 97 kilobars reported by Riggleman and Drickamer (1963).

X-ray diffraction patterns of the high-pressure area show it to be a mixture of the *rock salt* phase plus some other phase. Even when the force is increased until the *100 kilobar* phase boundary spreads out almost to the edges of the anvil faces, the *rock salt* phase continues to be present in the center of the sample area. When the sample is retained by a brass gasket so that it cannot flow outward, the *x*-ray diffraction pattern shows no lines of the *rock salt* phase at pressures above the phase transformation. This situation would arise if the shear strength of the new phase is so low that it is unable to sustain a pressure gradient. The *x*-ray diffraction pattern of the *100 kilobar* phase (Table 2) is not that of a cubic substance. Attempts to index it uniquely in one of the other systems were not successful.

STABILITY FIELDS OF THE POLYMORPHS

Triple points and boundaries of stability fields can be determined by visual observations with the high pressure diamond cell. The movement of a phase boundary toward the center of the sample area with increasing

TABLE 2. *X*-RAY DATA FOR THE 100 KILOBAR PHASE OF SILVER IODIDE

I/I_{10}	d(Å)
10	2.879
3	2.656
2	2.471
1	2.337
4	2.112
4	1.983
2	1.668
2	1.442
1	1.4165
1	1.3235
3	1.2925
3	1.1792

temperature indicates an increase of transformation pressure with increasing temperature, *i.e.* a positive slope of the boundary plotted on a pressure-temperature plane. Outward motion of a boundary in the sample indicates a negative slope. When a triple point is reached, a third phase is seen to appear or disappear at the boundary between two other phases.

Lower-Triple Point. The temperature of the triple point where the *wurtzite*, *3 kilobar*, and *rock salt* phases coexist has been determined with the present technique by measuring the temperature of the appearance and disappearance of the *3 kilobar* phase as the temperature was raised and lowered. It was found that the appearance and disappearance of the *3 kilobar* phase could be made to occur more promptly by rapid cycling of the pressure as the temperature was slowly changed. This technique has yielded a mean temperature of 65 ± 2° C. The uncertainty for the individual determinations of temperature is better than ±0.3° C. and the remainder of the uncertainty results from the spread of determinations. This determination is in good agreement with Duecker's value of 63° C. obtained by holding the temperature for periods of hours (pers. comm.).

The phase boundary between the *wurtzite* and *3 kilobar* stability fields has been determined to be parallel to the temperature axis between 25° C. and 65° C. The lower triple point, therefore, occurs at the same pressure as the phase transformation at 25° C. which in turn has been determined to be 3.1 ± 0.4 kilobars. The phase boundary between the *3 kilobar* and *rock salt* phases has a negative slope and extends from 4.0 ± 0.4 kilobars at 25° C. to the lower triple point (Fig. 1).

Upper Triple Point. The temperature of the upper triple point at which the *wurtzite*, *rock salt*, and *body-centered cubic* phases coexist has been determined by the same technique and the value obtained is 98 ± 2° C. The phase boundary between the *wurtzite* and *rock salt* phases has been determined to be parallel to the temperature axis between 65° C. and 98° C. The upper triple point, therefore, occurs at the same pressure as the lower triple point which in turn has been determined to be 3.1 ± 0.4 kilobars. These values for the temperature and pressure of the upper triple point are in good agreement with those of Bridgman (1915) at 99.4° C. and 2.76 kilobars.

Lieser (1958) examined the effect of pressure on the boundary between the *wurtzite* and *body-centered cubic* phases up to 70 atmosphere pressure by electric resistivity and obtained a value of −15.2° C./Kb. Majumdar and Roy (1959), on the other hand, obtained a value of −14.7° C./Kb by means of differential thermal analysis techniques under pressure. If the phase boundary is a straight line between the transformation temperature at atmospheric pressure and the triple point, the results of the present

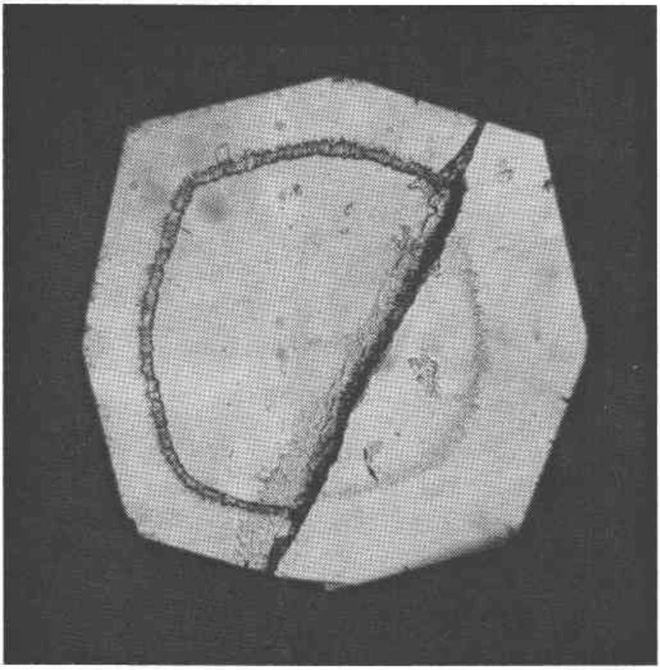

FIG. 9. Silver iodide (left) and rubidium chloride (right) placed side by side in the diamond cell. The optical discontinuity in rubidium chloride represents the 5.3 kilobar transformation. On the left the *3 kilobar* phase of silver iodide is seen as a dark ring.

study would yield a value of −15.5° C./Kb, which is in fair agreement with the previous determinations. However, the slight discrepancy may be caused by a slight curvature of the phase boundary.

100 Kilobar Phase Boundary. The 100 kilobar phase boundary appears to be parallel to the temperature axis, but this cannot be stated with certainty because of the sluggish response of the phase boundary to changes in pressure.

EFFECT OF PRESSURE ON THE LATTICE DIMENSIONS AND INTERATOMIC DISTANCES

The effect of pressure on the lattice dimensions, interatomic distances and molar volumes of various polymorphs of silver iodide are of crystallochemical and thermodynamic interest since the volume change is directly related to the Gibbs free energy. The molar volume of a substance under given temperature-pressure conditions can be calculated from the lattice dimensions when its crystal structure is known.

Sodium chloride mixed with the sample serves as a pressure internal standard. The pressure dependency of its molar volume has been accurately determined by Bridgman (1945) up to 40 kilobars and by Christian (1957) up to 200 kilobars at 25° C. The pressure to which the silver iodide is subjected can be calculated from the molar volume of the sodium chloride.

For the accurate determinations of the lattice dimensions as a function of pressure, the geometry of the *x*-ray camera must not change due to mechanical deformation of the parts under pressure. The sample-to-film distances are reproducible to within 0.3 per cent before and after a series of runs including ones over 100 kilobars (Bassett and Takahashi, 1965). The effect of elastic deformation of the anvils and other parts on the sample-to-film distance is probably negligible. The over all accuracy of the present data is ±0.3 per cent in the lattice dimensions, ±1 per cent in the molar volumes, and ±5 per cent in the pressure measurements.

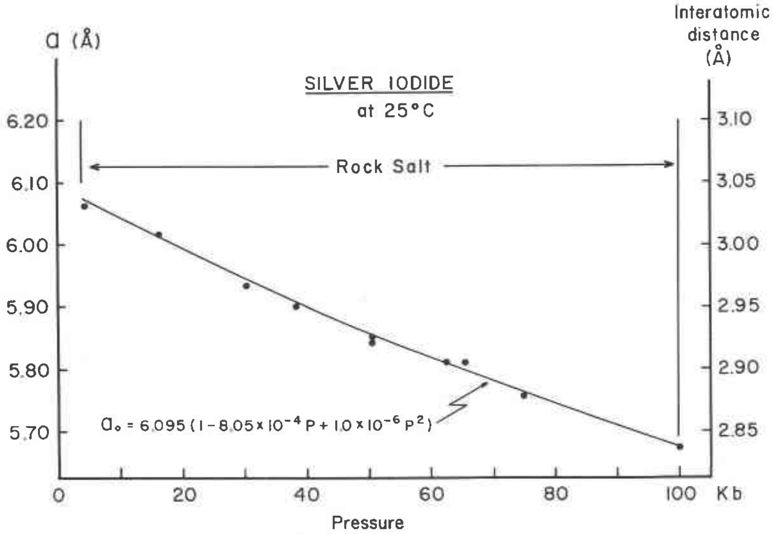

FIG. 10. The unit cell edge (*a*) and the Ag^+ to I^- distance in the *rock salt* phase of silver iodide as a function of pressure at 25° C. An empirical equation for the curve is given.

The lattice dimension of the *rock salt* phase of silver iodide has been determined at 25° C. as a function of pressure within its stability field between 4 and 100 kilobars. It decreases from 6.07 Å at 4 kilobars to 5.67 Å at 100 kilobars (Figure 10), and may be expressed by an empirical equation: $a\ (A)=6.095\ (1-8.05\times10^{-4}\ P+1.0\times10^{-6}\ P^2)$, where P is in kilobars and $4\leq P\leq 100$ kilobars. In the *rock salt* structure, the interatomic distance of the nearest neighbors is equal to half of the lattice dimension, and is also plotted in Fig. 10. Jacobs (1938a) obtained 6.070 Å at 3.3 kilobars and room temperature and Piermarini and Weir (1962) obtained 6.067 under the same conditions. The present results at 4 kilobars are in good agreement with those of the previous workers.

The effect of pressure on the molar volume can readily be obtained from the lattice dimension, Avogadro's number and the number of atoms per unit cell: $V = 34.09\ (1 - 2.4 \times 10^{-3}\ P + 5 \times 10^{-6}\ P^2)$, where V is in cubic centimeters per mole, P in kilobars, and $4 \leq P \leq 100$ kilobars. The molar volume decreases from 33.80 cm^3/mole at 4 kilobars to 27.60 cm^3/mole at 100 kilobars. The results are plotted in Figure 11 along with the data of Bridgman (1945), which were corrected according to the revised pressure scale of Kennedy and LaMori (1961). The molar volumes obtained by Bridgman appear to be consistently 0.9 per cent higher than the results of this work, whereas the slopes of the compression curves are in good agreement.

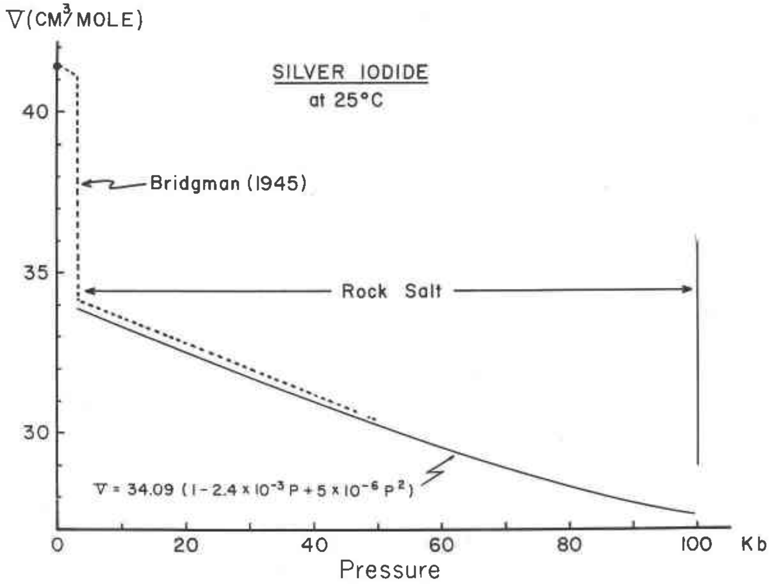

FIG. 11. The molar volume of the *rock salt* phase of silver iodide as a function of pressure at 25° C. An empirical equation for the curve is given. Bridgman's values which are corrected according to Kennedy and LaMori (1961) are plotted for comparison.

PHASE TRANSFORMATIONS AND CRYSTAL STRUCTURES

Since Bridgman's pioneering work on the volumetric and electrical resistance determinations of pressure-induced polymorphs, the crystal structures of a number of the high pressure polymorphs of elements and compounds originally studied by him have been determined by *x*-ray diffraction techniques. The binary compounds of ionic nature such as potassium iodide, rubidium chloride, rubidium iodide, rubidium fluoride and sodium chloride which have the *rock salt* structure transform to the *cesium chloride* structure under high pressures as determined by Jacobs (1938b), Guegant and Vodar (1954), Jamieson (1957), Piermarini and Weir (1962, 1964) and Evdokimova and Vereshchagin (1963). On the other hand, binary compounds with non-ionic bonding such as lead sulfide, selenide, and telluride which have the *rock salt* structure transform under high pressure to the *tin sulfide* (distorted *rock salt*) structure with orthorhombic symmetry (Takahashi *et al.*, 1964). Apparently, therefore, binary compounds with the *rock salt* structure at atmospheric conditions transform to the *cesium chloride* structure at high pressures, if the nature of their bonding is ionic, but may transform to a complex structure if the bonding is non-ionic. Mayer (1933) evaluated the lattice energy of silver iodide assuming ionic bonding with a van der Waals potential, and concluded that the bonding in silver iodide is not purely ionic but that approximately 10 per cent of the lattice energy is due to covalent bonding. Both Jacobs (1938b) and Huggins (1951) reached a similar conclusion by using more refined data on the polymorphic transformation and lattice parameter. Pauling's evaluation of the electronegativities of silver and iodine (1.9 and 2.5 respectively) indicates extensive covalent bonding in silver iodide. In silver iodide the rock salt phase does not transform to a phase having the *cesium chloride* structure above 100 kilobars at room temperature. Instead, it transforms to a phase giving a complex noncubic *x*-ray diffraction pattern. This may be due to unequal bond strengths in contrast to the bonding in ionic compounds. These findings are consistent with the other indications that the bonding in silver iodide is covalent.

A number of theoretical studies (an excellent review by Tosi, 1964) have been made to explain and/or postulate the stabilities of various polymorphs of AX type metal halides including silver iodide by estimating the lattice energies for the *sphalerite*, *rock salt*, and *cesium chloride* type structures. However, in spite of those theoretical efforts, all attempts have failed to account for the observed pressure-temperature stability fields for polymorphs in even simple ionic crystals (*e.g.* Born and Huang, 1954, p. 162). Further knowledge of the stability range of polymorphs, lattice dimensions, crystal structures, and compressibilities would obviously contribute to the better understanding of the fundamental nature of bonding.

SUMMARY AND CONCLUSIONS

A diamond anvil cell has been used for the study of the phase relations, crystal structures and compressibilities of polymorphs of silver iodide under pressure-temperature conditions exceeding 100 kilobars and 200° C. The techniques described may be widely applicable to the determinations of stability fields of polymorphs of many other compounds. The conclusions are summarized as follows.

1) The *sphalerite* phase appears to have no thermodynamic stability field over the pressure-temperature range of the present investigation.
2) The stability field of the *3 kilobar* phase has been determined. The triple point at which the *3 kilobar*, *wurtzite*, and *rock salt* phases coexist lies at 3.1 ± 0.4 kilobars and 65 ± 2° C.
3) At 25° C. the *rock salt* phase is stable between 4.0 ± 0.4 kilobars and 100 ± 5 kilobars. Its lattice dimension decreases from 6.07 Å at 4 kilobars to 5.67 Å at 100 kilobars, and the molar volume from 33.80 cm^3/mole at 4 kilobars to 27.60 cm^3/mole. Empirical equations for the effect of pressure on those parameters have been derived.
4) At 100 ± 5 kilobars and 25° C., the *rock salt* phase transforms to still another high pressure form. Although a clear *x*-ray diffraction pattern of the 100 kilobar phase has been obtained, it cannot be indexed as a cubic structure.
5) The lattice energy and lattice dimension of the *rock salt* phase calculated by assuming ionic bonding differ considerably from the experimental values, indicating the covalent nature of the bonding.

ACKNOWLEDGMENTS

This investigation was supported by a grant from the National Science Foundation (Number GP 3255).

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