rent is kept constant a state is rapidly attained in which conditions at the growing tip remain the same.

If q coulombs of charge are passed through the cell, and if the current through the cell consists entirely of the transport of metal ions, and if a metallic dendrite of mean cross-section $\bar{a}$ (cm^2) is formed, its length x will be:

$$x = \frac{eq}{F\rho\bar{a}} \qquad (1)$$

where e is the chemical equivalent of the metal, ρ its density, and F is the Faraday (96,500 coul).

A current of I amperes will cause the dendrite to grow at a rate

$$\frac{dx}{dt} = \frac{eI}{F\rho\bar{a}} \qquad (2)$$

If the cathode is connected to the anode by way of a tube of uniform cross-section a (cm^2) and length x_0 (cm), filled with electrolyte of conductivity σ (mho cm^{-1}), the resistance of the cell will then be

$$R = R_0 + \frac{x_0 - x}{\sigma\, a} \qquad (3)$$

where R_0 is the resistance of the rest of the cell excluding the tube. The rate of change of resistance of the cell when a current I flows through it is

$$\frac{dR}{dt} = -\frac{1}{a\,\sigma}\ \frac{dx}{dt} = -\ \frac{eI}{F\rho\sigma a\bar{a}} \qquad (4)$$

Equation 2 can be rewritten in order to yield a quantity which can be measured. We define a quantity G which expresses the increase in the length of the dendrite in centimeters when 1 coul of charge is passed through the cell:

$$G = \frac{1}{I}\ \frac{dx}{dt} = \frac{e}{F\rho\bar{a}} \qquad (5)$$

Since this quantity depends upon the mean cross-section of the dendrite, the value of G may be taken as a continuous measure of the "type" of dendrite.

Figure 2 shows G as a function of current and concentration for the growth of silver dendrites in a cell containing silver nitrate electrolyte and silver electrodes. For an electrolyte of given concentration, the transition point between the type of crystal which almost fills the tube (formed by relatively low currents) and the true dendritic type is quite sharp. The current at which this point occurs is greater for higher concentrations, agreeing with the qualitative considerations discussed earlier.

The peculiar electrical and geometrical properties of a narrow tube filled with an electrolyte permit not only the controlled growth of metallic dendrites, but also their controlled dissolution. The dendrites do not dissolve entirely; small pieces break off and fall to the bottom of the tube. Nevertheless, the resistance of the tube does change fairly smoothly (Fig. 3). This contrasts with the dissolution of dendrites grown in unrestricted electrolytes where the resistance of the cell often changes instantaneously to its maximum value.

The curves of Fig. 3 were obtained by measuring the resistance of the cell as a function of time while the current was passed in one direction for a given amount of time, then reversed for the same amount of time. After about five reversals the process stabilizes, and the resistance goes through reproducible cycles.

A need has been felt by the designer of adaptive machinery for a small, inexpensive component whose electrical properties can be adjusted automatically (*7*). It is possible that electrochemical cells of the design of Fig. 1 may fulfill this need (*8*).

The linear variation of resistance with time, coupled with the possibility of resistance changes in either direction, make these cells particularly attractive. The resistance of a cell can be "read" nondestructively with an a-c signal.

Cells with tubes about 1 mm in diameter and about 10 cm long have resistances of 1 to 100 kohm, which makes them suitable for incorporation into conventional electronic circuits. With these dimensions the time required for a reasonable change in resistance is of the order of minutes, which may seem rather long. By reducing the physical dimensions of the capillaries, advantage may be taken of the rapid axial growth rate in narrow channels (*8*). Because the resistance range of the cell remains approximately the same as long as the ratio of length to cross section of the tube remains the same, miniaturization of this cell permits the design of quickly responding elements with appropriately matched impedances for use in large adaptive systems.

W. A. AINSWORTH

Department of Electrical Engineering, University of Illinois, Urbana

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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

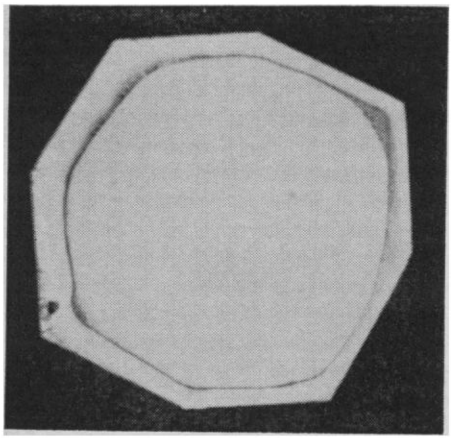

Fig. 1. Silver iodide in diamond anvil high-pressure cell at an applied pressure of 4 kb (× 100).

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, requiring 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.

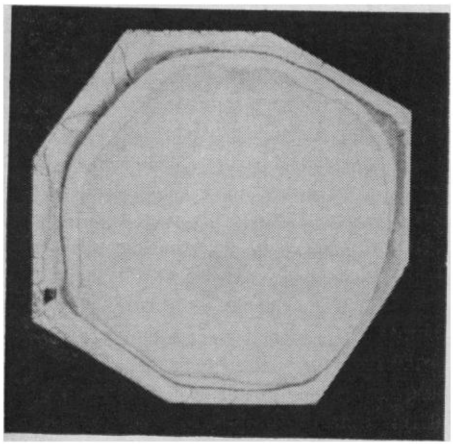

Fig. 2. Sample in Fig. 1 with pressure reduced to 3 kb.

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 5×10^{-6} ohm^{-1} cm^{-1}, while the material in the region of the black band had a conductivity of 1.9×10^{-3} ohm^{-1} cm^{-1}. Baranovskii *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 thermal 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.

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*

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 cm^3 mole^{-1}, while the volumes of free silver and iodine at this pressure are 10.24 cm^3 g-atom^{-1} and 25.59 cm^3 mole^{-1}, respectively. The total, 35.83 cm^3 mole^{-1}, is larger than the volumes of a proposed orthorhombic phase (*6*) (35.64 cm^3 mole^{-1}) and the NaCl phase at 3 kb (35.28 cm^3 mole^{-1}). These volume relations are thermodynamically consistent and give further support to the 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

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High Pressure Polymorphism in Cesium

Abstract. *A new polymorph of cesium, existing over the narrow pressure range from about 42.2 to 42.7 kilobars at room temperature, has been discovered. Its crystal structure is face-centered-cubic with* a = *5.800 ± 0.007 Å at 42.5 kb and 27°C. Cesium-II, which exists over the pressure range 23.7 to 42.2 kb, is also face-centered-cubic with* a = *5.984 ± 0.011 Å at 41 kb and 27°C. An improved resistance-pressure curve and x-ray compressibility measurements for Cs are also given.*

By displacement and electrical resistance measurements Bridgman (*1*) discovered several pressure-induced transitions in cesium metal. Volume transitions were reported to occur at about 23 kb with relative volumes v/v_0 of 0.6284 and 0.6224 (uncompressed Cs being 1.0000) and at about 45 kb with relative volumes of 0.498 and 0.442. We have obtained the relative volumes at 45 kb by interpolation from Bridgman's data. Bridgman gives data as compressions and also as volumes (relative volumes). The compressions at 23 kb given by Bridgman have been converted to relative volumes by subtracting his compression values from unity.

Bridgman found a resistance transition at about 23 kb and identified it with the corresponding volume transition. He also found a sharp resistance cusp at about 55 kb. Bridgman presented arguments for and against this transition's being identified with the volume transition at 45 kb without coming to any conclusion. Kennedy and LaMori (*2*) proposed that Bridgman's resistance cusp was caused by the same transition responsible for the large volume decrease at 45 kb and that the pressure given for Bridgman's resistance transition was 10 kb too high. They determined (by piston displacement) the pressures required to obtain the two volume transitions in Cs as 22.6 ± 0.6 kb and 41.8 ± 1.0 kb, respectively. However, volume changes occurring at the transitions were not reported.

Kennedy, Jayaraman, and Newton (*3*) determined the fusion curve and stability regions for Cs phases to 50 kb. Bundy (*4*) measured the electrical resistance of Cs in the Belt apparatus and, after correcting Bridgman's data to the "new" pressure scale, obtained essentially the same curve. Stager and Drickamer (*5*) also measured the electrical resistance of Cs in a supported flat anvil device. They discovered a new transition starting at about 175 kb (sharp resistance rise of about 200 percent) and observed Bridgman's 45 kb cusp to occur at apparent pressures ranging from 20 to 70 kb. Hall (*6*) measured the electrical resistance of Cs as a function of pressure, using the cusp as a pressure calibration point for the Belt apparatus, and obtained a curve considerably different from the other curves that have been reported, the sweeping cusp being replaced by one resembling a spike.

A resistance curve has also been determined in the tetrahedral press which has excellent resolution. This device clearly shows a spike, with an essentially flat top, 0.5 kb wide (Fig. 1). For comparison, Bridgman's original curve is also given. The present determination was made by four-lead resistance measurement techniques on Cs metal contained in a polyethylene tube (approximately 0.63 cm long × 0.050 cm inside diameter × 0.076 cm outside diameter) embedded in a silver chloride slug, which, in turn, was centered within a pyrophyllite tetrahedron. The temperature was 25°C. Readings were taken with increasing pressure for the curve shown. The flat-topped spike clearly indicates the presence of a formerly unsuspected phase. We will call this phase Cs III and, for the present, label the phase (or phases) just to the right of the spike "Cs IV." A calibration (*7*) for the tetrahedral press with the fixed transition points Bi I-II, 25.3 kb; Tl I-II, 37.0 kb; Ba I-II, 59.0 kb, gives the Cs transition points (from the resistance curve) as follows: Cs I-II, 23.7 kb; Cs II-III, 42.2 kb; Cs III-"IV", 42.7 kb.

Table 1. X-ray diffraction data for face-centered-cubic Cs II at 27°C and 41 kb. Average *a* (with average deviation from the mean) = 5.984 ± 0.011 Å; v/v_o = 0.455. The calculated intensities (*I*) include multiplicity, structure, and Lorentz polarization factors, but do not include absorption or temperature factors.

hkl	*d*	*a*	I_{exp}*	I_{calc}
111	3.456	5.986	318†	100
200	2.996	5.991	51	51
220	2.105	5.953	42	41
311	1.808	5.997	54	55
222	1.727	5.982	16	16
400	1.499	5.998	vw‡	7
331	1.375	5.993	22	23
420	1.335	5.972	16	20

* Integrated intensity. † The (111) line exhibited an unusually high intensity. The observed relative intensities are based on (200) = 51. ‡ Very weak.

An interesting feature was disclosed on investigating the resistance curve over the temperature range of 24 to 31°C. On cycles of increasing pressure, the curve is identical with that shown in Fig. 1. Also, on reducing pressure the resistance curve faithfully retraces the characteristics of the forward curve (with attendant hysteresis due to pyrophyllite), clearly showing the spike and other features as long as the temperature is above 26.0° ± 0.4°C. However, at temperatures below 26.0° ± 0.4°C, on cycles of decreasing pressure, the Cs III phase is by-passed; "Cs IV" apparently transforms di-