

## High-pressure phase diagram of silver mercury iodide ( $\text{Ag}_2\text{HgI}_4$ )

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Differential scanning calorimetry has been used to study the phase diagram of  $\text{Ag}_2\text{HgI}_4$  in the range up to 1 GPa and from 278 to 440 K. Stoichiometric samples were prepared by a solid-state reaction which gives pure  $\text{Ag}_2\text{HgI}_4$ , while previous high-pressure studies have been on samples prepared by precipitation, a technique where the presence of minor amounts of AgI as impurity hardly can be avoided. The phase diagram is characterized by two triple points: 0.477 GPa, 328.5 K and 0.74 GPa, 400.5 K. At ambient temperature a transition between the ordered phases occurs at 0.62 GPa when the pressure is increased but at 0.47 GPa when the pressure is decreased. In both cases the transition enthalpy is strongly temperature dependent, indicating that there is either a triple point or a critical point near 270 K. The temperature of the order-disorder transition between the  $\beta$  and  $\alpha$  phases increases from 325 K at normal pressure to a maximum of 334 K at 0.42 GPa. The enthalpy of the  $\beta \rightleftharpoons \alpha$  transition is 8.5 kJ/mol at normal pressure and 6.2 kJ/mol in the range 0.0001–0.477 GPa. The enthalpy of the  $\gamma \rightleftharpoons \alpha$  order-disorder transition increases from 1.3 kJ/mol at 0.477 GPa to 6.8 kJ/mol at 0.74 GPa. Perhaps the most remarkable features of this phase diagram concern the transition of the disordered  $\alpha$  phase to other disordered high-temperature phases. At normal pressure the transition enthalpy is 11.5 kJ/mol at 425 K. The transition temperature has a maximum of 428 K at about 0.045 GPa. At higher pressures the transition changes its character, and it is clearly second order from, say, 0.16 GPa to a singularity point (minimum) at 0.474 GPa and 382 K. Beyond this point the transition enthalpy increases linearly from zero up to 11.9 kJ/mol at 0.74 GPa.

### I. INTRODUCTION

Silver mercury iodide,  $\text{Ag}_2\text{HgI}_4$ , has attracted much interest due to its unusual electrical and optical properties. It is one of the first studied examples of a thermochromic material, as when heated, its color changes from yellow to red in the vicinity of 50° C. It was found more than a century ago that this color change was associated with a discontinuous change of the volume,<sup>1</sup> and a series of studies by Katelaar showed *inter alia* that there was a drastic change in the electrical conductivity<sup>2</sup> which was due to an order-disorder transition of the cations.<sup>3</sup> Since then the disordered  $\alpha$  phase has been one of the classical examples of a solid electrolyte or superionic conductor. The present views on the structure of the two phases have been summarized recently.<sup>4</sup>

Most of the numerous investigations have been made at normal pressure, but some properties have been studied also at high pressure. These works have not, however, resulted in an acceptable phase diagram. The published results are fragmentary and often controversial. The first tentative phase diagram was obtained by Weil and Lawson<sup>5</sup> from ac-conductivity measurements on pellets of salt that were prepared by precipitation.<sup>3</sup> Hydrostatic conditions up to 0.8 GPa were realized in a liquid environment, and the pressure was determined by means of a calibrated Manganin coil. Their measurements were carried out at four different temperatures (25, 43, 64.5, and 83.5°C), and in all cases the conductivity had a maximum around 0.4 GPa and it changed abruptly around 0.6 GPa.

This was taken as indicative of phase transitions at both pressures.

The pressure conditions were much less accurate in Webb's study,<sup>6</sup> where either a tetrahedral anvil press or a diamond anvil cell was used, which means that there were pressure gradients in the ungasketed diamond anvil working volume. Furthermore, the pressure scale was calibrated only by means of some known phase transitions. As in the previous study,<sup>5</sup> peculiarities in the course of the electrical conductivity as a function of pressure were taken as indicative of phase changes. In this way the reported<sup>5</sup> transitions at 0.4 and 0.6 GPa were confirmed, and additional ones were found at 0.75, 4.4, and 7.5 GPa. Quantitatively, the agreement between the conductivity results of the two studies<sup>5,6</sup> was poor. Optical observations were also made in the diamond anvil cell for which only the central part of the working volume was considered to be of importance for studying phase transitions. This central part was calibrated by different optically observable transitions of some inorganic salts. Only an approximate agreement could be found with respect to the pressure ranges of the different phases as compared with the conductivity measurements. Different colors were taken as characteristic for the five phases mentioned above. It is remarkable that the phase existing between 0.4 and 0.6 GPa was not significantly different from the one below 0.4 GPa. We shall come back to this statement when discussing our results. All observations described correspond to room temperature.<sup>6</sup>

No phase transitions were found by Shibata *et al.*<sup>7</sup> by

investigating the electrical conductivity of pressed pellets in the temperature range 286–351 K and for pressures up to 0.3 GPa. But, on the other hand, if a minimum of electrical conductivity is to be treated as an indication of a phase transition, as in Webb's paper,<sup>6</sup> a transition around 0.1 GPa could be deduced from the results (see Fig. 4a of Ref. 7) in the temperature range 333–351 K for the  $\alpha$  phase of  $\text{Ag}_2\text{HgI}_4$ . The absence of further phase transitions is obviously due to the limited pressure range applied. The pressure dependence of the  $\beta \rightarrow \alpha$  transition temperatures is given up to 0.2 GPa.

Contrary to previous observations,<sup>5,6</sup> no phase transition was found around 0.4 GPa by Greig *et al.*,<sup>8</sup> who studied Raman spectra changes. However, the transition around 0.6 GPa was confirmed for both the  $\alpha$  and the  $\beta$  phase, in agreement with the previous electrical conductance and optical observations.<sup>5,6</sup> Narrow band widths and the spectral simplicity of the phase above 0.6 GPa are taken as indicative for the ordered state of this phase. Unfortunately, the latter authors do not give any information about the samples used. As we will discuss later, the details of the preparation method are crucial for an objective comparison of results achieved in different laboratories.

A combination of electrical conductivity, differential thermal analysis, x-ray diffraction, and optical-absorption measurement were used in a recent paper<sup>9</sup> for determining the boundaries of the high-pressure phase diagram. Since a tetrahedral press and a belt anvil were applied, no accurate results were claimed below 0.8 GPa, only a tentative confirmation of the 0.6 and 0.4 GPa transitions observed previously.<sup>5,6</sup> Furthermore, transformations were found at 0.8, 2.0, and 3.6 GPa.

Two recent papers were devoted to Raman scattering and electrical conductivity at high pressures.<sup>10,11</sup> Some optical microscopic observations gave additional evidence of phase transitions, but these were carried out under nonhydrostatic conditions by using an insufficiently gasketed diamond anvil cell. This type of high-pressure device was applied in both papers. The existence of a phase transition around 0.4 GPa at room temperature is clearly denied in one paper<sup>10</sup> (as in the first Raman study<sup>8</sup>) but seems to be confirmed in the other one.<sup>11</sup> This controversy will be discussed later in connection with our results. As in all previous papers the transition around 0.6 GPa at room temperature was confirmed.<sup>10,11</sup> Furthermore, a transformation at 0.81 GPa was found.<sup>11</sup>

The purpose of our present paper is to establish the phase diagram for exactly stoichiometric silver mercury iodide in the temperature range 278–430 K and for pressures up to 1 GPa, using differential scanning calorimetry (DSC). In this way phase transitions exhibiting enthalpy or heat-capacity changes could be detected, provided the kinetics are suitable. Each transition was characterized by its temperature, taken from the slope of the heat-capacity time curve, and the enthalpy change determined from the integral of the heat-capacity time course. Furthermore, the volume changes could be calculated from the slope of the phase boundary and the enthalpy change measured, using the Clausius-Clapeyron relation. A special feature of high-pressure DSC is that the sign of the slope  $dT/dp$

of a phase boundary can always be determined for the first-order phase transition by increasing the pressure isothermally. If an exothermic enthalpy change (heat given off) is observed, this means that  $dT/dp > 0$ , and vice versa.

DSC gives much more accurate information on transition enthalpies than the more commonly used differential thermal analysis (DTA) procedure does. DSC records the energy that is required to keep both sample and reference at the same temperature when the sample undergoes a phase transition, while DTA records the temperature difference between sample and reference during the transition. A brief report of some of our results has been given previously.<sup>12</sup>

## II. EXPERIMENTAL METHOD

As in our previous investigations<sup>13–15</sup> commercial DSC equipment from Rigaku (Japan) was used. Its sample holder (which also contains the reference sample) was placed in the high-pressure vessel. Details of this modification as well as the standardization procedure are described elsewhere.<sup>16–18</sup> Basset-Bretagne-Loire high-pressure equipment served our purposes with gaseous argon as the pressure transmitting medium. Thus hydrostatic conditions were assured. The pressure was measured by a calibrated Manganin gauge with an accuracy better than 5 MPa. Stoichiometric samples were prepared by a solid-state reaction between weighed powders of silver and mercury iodides. As a criterion for stoichiometry, the DSC characteristics were taken for the order-disorder transition at normal pressure, whereby three conditions had to be fulfilled.

(1) There should be only one transition peak, i.e., no indication of even a minute excess of either of the initial components.

(2) The transition temperature must exhibit the maximum value observed that is 325 K if taken from the slope of the rising peak.

(3) The transition enthalpy should be equal to about 8.5 kJ/mol.

Further details of this procedure as well as the importance of the sample preparation have been stressed before,<sup>14,15,19</sup> and will be discussed later on in this paper. Depending on the part of the phase diagram investigated, either a temperature (at nearly constant pressure) or a pressure (at nearly constant temperature) scan or both, were used. Scanning and recording rates were chosen in such a way that the obtained transition peaks were suitable for determining both the transition temperature and the enthalpy as accurately as possible.

## III. RESULTS AND DISCUSSION

### A. General presentation of the phase diagram

The resulting phase diagram is presented in Fig. 1, and the numerical data characterizing its details are given in Table I. The following linear relations have been used for the temperature  $T$  (K), the transition enthalpy  $\Delta H$  (kJ/mol), and the volume change  $\Delta V$  ( $\text{cm}^3/\text{mol}$ ) as a function of pressure  $p$  (MPa) or, alternatively, of temperature:

$$T(p) = T_0 + (dT/dp)(p - p_0), \quad (1)$$

$$\Delta H(p) = \Delta H_0 + (d\Delta H/dp)(p - p_0), \quad (2)$$

$$\Delta H(T) = \Delta H_0 + (d\Delta H/dT)(T - T_0), \quad (3)$$

$$\Delta V(p) = \Delta V_0 + (d\Delta V/dp)(p - p_0). \quad (4)$$

The volume change is calculated by means of the Clausius-Clapeyron equation from the transition enthalpy and the slope of the phase boundary  $dT/dp$ . Contrary to all previous investigations mentioned in the Introduction, our results were taken in pressure steps not larger than 0.02–0.03 GPa and temperature steps of about 5°. Therefore we give all phase boundaries as continuous lines without the individual measurements. All phase boundaries indicated were traced several times in different time sequence.

As shown in Fig. 1, in the pressure-temperature ranges considered, four different phases can be distinguished: the  $\beta$  phase, stable at ambient temperature and pressure conditions and exhibiting an ordered tetragonal structure, the  $\alpha$  phase with the same iodide sublattice but fully disordered silver and mercury sublattices (this phase exhibits a high ionic conductivity), the  $\gamma$  phase, probably another ordered phase stable only at high pressure (it has been suggested<sup>5</sup> that this phase has the same rocksalt structure as the high-pressure fcc phase of AgI), and, finally, the  $\delta$  phase at the highest temperatures studied by

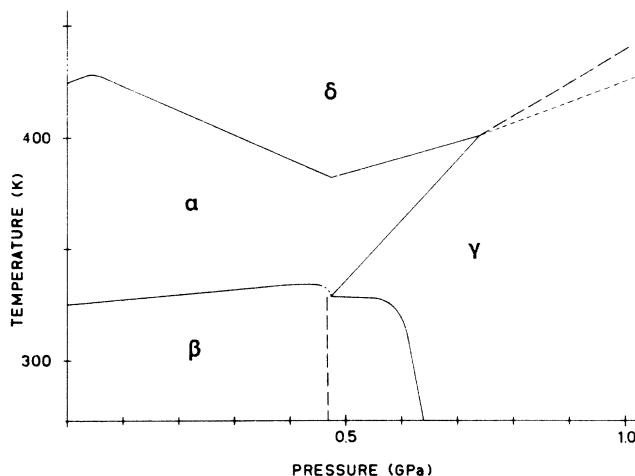


FIG. 1. Phase diagram of  $\text{Ag}_2\text{HgI}_4$ . Concerning the high-temperature region ( $\delta$ ), we have not attempted to search for a transition between a suggested hexagonal phase, denoted  $\text{AgHgI}_3$ , and the bcc phase  $\alpha\text{-AgI}$ , cf. Ref. 21. Concerning the nearly vertical boundary between the  $\beta$  and  $\gamma$  phases, the solid line corresponds to increasing pressure, and the dotted-dashed one to decreasing pressure. Regarding the boundary between the  $\gamma$  and  $\delta$  phases, the long-dashed line is calculated from the conditions at the triple point, while the short-dashed line is experimental, obtained by increasing the pressure at constant temperature.

TABLE I. Phase transitions of silver mercury iodide,  $\text{Ag}_2\text{HgI}_4$ . The phases are identified with greek letters as shown in Fig. 1. The linear relations of Eqs. (1) to (4) have been applied when possible. Units: temperature  $T$  in K; pressure  $p$  in MPa; transition enthalpy (latent heat),  $\Delta H$ , in kJ/mol; volume change  $\Delta V$  in  $\text{cm}^3/\text{mol}$ . Sign convention:  $\Delta H = H_2 - H_1$  and  $\Delta V = V_2 - V_1$ , where the subscript 1 denotes the low- and 2 the high-temperature phase.

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|---|
| Order-disorder transition between the $\beta$ and $\alpha$ phases:<br>0.1 to 477 MPa  |
| $T(p) = 325 \pm 0.5 + (21.6 \pm 1.4)10^{-3}p$ K for 0.1 to 360 MPa<br>$T = 334$ K at 420 MPa (maximum)<br>$\Delta H = 8.5 \pm 0.4$ kJ/mol and $\Delta V = 0.56$ $\text{cm}^3/\text{mol}$ at 0.1 MPa<br>$\Delta H = 6.2 \pm 0.3$ kJ/mol for 1–477 MPa<br>$\Delta V = 0.4$ $\text{cm}^3/\text{mol}$ for 1–420 MPa |
| Transition from the $\beta$ to the $\gamma$ phase:<br>section from 477 to 540 MPa   |
| $T \approx 328.5$ K<br>$\Delta H(p) = 5.0 \pm 0.3 - (3.2 \pm 0.4)(p - 477)10^3$ kJ/mol<br>$\Delta V \approx -0.1$ $\text{cm}^3/\text{mol}$  |
| Transition from the $\beta$ to the $\gamma$ phase:<br>section from 610 to 640 MPa (increasing pressure)   |
| $T(p) = 311.0 - 1.1(p - 610)$ K<br>$\Delta H(T) = 0.037 + 0.0106(T - 273.0)$ kJ/mol<br>$\Delta V = -1.9$ $\text{cm}^3/\text{mol}$ at 610 MPa and 311 K<br>$\Delta V = -0.2$ $\text{cm}^3/\text{mol}$ at 640 MPa and 278 K   |
| Transition from the $\gamma$ to the $\beta$ phase<br>(decreasing pressure)  |
| Approximately constant pressure 465–470 MPa for 278 to 318 K<br>$\Delta H(T) = 0.0108 + 0.0271(T - 273)$ kJ/mol   |

TABLE I. (Continued).

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|---|
| Order-disorder transition between the $\gamma$ and the $\alpha$ phases:<br>477 to 740 MPa   |
| $T(p) = 329.5 \pm 1.0 + (0.267 \pm 0.008)(p - 477)$ K<br>$\Delta H(p) = 1.28 \pm 0.31 + (0.0209 \pm 0.0023)(p - 477)$ kJ/mol<br>$\Delta V(p) = 1.27 \pm 0.24 + (0.0129 \pm 0.0016)(p - 477)$ cm <sup>3</sup> /mol   |
| Transition between the $\alpha$ and the $\delta$ phases:<br>section below 474 MPa   |
| $T = 425$ K at 0.1 MPa<br>$T = 428$ K at 45 MPa (maximum)<br>$T = 428.0 \pm 0.5 - (0.112 \pm 0.002)(p - 60)$ for $60 < p < 477$ MPa<br>$\Delta H = 11.5$ kJ/mol at 0.1 MPa<br>$\Delta H = 0$ and $\Delta V = 0$ for $156 < p < 474$ MPa   |
| Transition between the $\alpha$ and $\delta$ phases:<br>singularity point at 474 MPa  |
| $T = 382$ K (minimum)<br>$\Delta H = 0$ and $\Delta V = 0$  |
| Transition between the $\alpha$ and $\delta$ phases:<br>section between 474 and 740 MPa   |
| $T = 382 \pm 0.5 + (0.069 \pm 0.004)(p - 474)$ K<br>$\Delta H(p) = (44.1 \pm 1.9)(p - 474)10^{-3}$ kJ/mol<br>$\Delta V(p) = (7.7 \pm 0.8)(p - 474)10^{-3}$ cm <sup>3</sup> /mol   |
| Order-disorder transition between the $\gamma$ and $\delta$ phases<br>(740 MPa to 1 GPa)  |
| $T(p) = 400.5 + 0.145(p - 740)$ K   |
| $\alpha, \beta, \gamma$ triple point at 477 MPa and $328.5 \pm 1.0$ K   |
| $\beta \rightarrow \alpha$ , $\Delta H = 6.2 \pm 0.3$ kJ/mol (expt.)<br>$\beta \rightarrow \gamma$ , $\Delta H = 4.9 \pm 0.3$ kJ/mol (expt.) and $\Delta V = -0.1$ cm <sup>3</sup> /mol<br>$\gamma \rightarrow \alpha$ , $\Delta H = 1.3 \pm 0.3$ kJ/mol (expt.) and $\Delta V = 1.3 \pm 0.3$ cm <sup>3</sup> /mol  |
| $\alpha, \delta, \gamma$ triple point at 740 MPa and $400.5 \pm 1.0$ K  |
| $\alpha \rightarrow \delta$ , $\Delta H = 11.9 \pm 0.5$ kJ/mol (expt.) and $\Delta V = 2.1 \pm 0.2$ cm <sup>3</sup> /mol<br>$\gamma \rightarrow \alpha$ , $\Delta H = 6.8 \pm 0.7$ kJ/mol (expt.) and $\Delta V = 4.7 \pm 0.9$ cm <sup>3</sup> /mol<br>$\gamma \rightarrow \delta$ , $\Delta H = 18.7$ kJ/mol (calc.) and $\Delta V = 6.8$ cm <sup>3</sup> /mol |

us. It has been suggested by Steger<sup>20</sup> that this phase is identical with the cation disordered bcc phase  $\alpha$ -AgI, where 50% of the Ag<sup>+</sup> ions are replaced by Hg<sup>2+</sup> ions and vacancies. A later study of the AgI-HgI<sub>2</sub> system<sup>21</sup> suggests that at normal pressure a hexagonal phase, AgHgI<sub>3</sub>, exists in a small temperature region between  $\alpha$ -Ag<sub>2</sub>HgI<sub>4</sub> and  $\alpha$ -AgI. At normal pressure the AgI-HgI<sub>2</sub> phase diagram has a maximum at 425 K for stoichiometric Ag<sub>2</sub>HgI<sub>4</sub> (similar to the maximum at 325 K for the order-disorder transition).<sup>20,21</sup> This indicates that the stoichiometric compound is stable just above the phase transition at 425 K.

There are two triple points. First between the  $\alpha$ ,  $\beta$ , and  $\gamma$  phases at 0.477 GPa and 329 K. Second between the  $\alpha$ ,  $\delta$ , and  $\gamma$  phases at 0.74 GPa and 400 K. Furthermore, there exists a singularity at the  $\alpha$ ,  $\delta$  boundary line at 0.474 GPa and 382 K and a marked decrease around 0.6 GPa

and 320 K at the  $\beta, \gamma$  phase boundary.

Let us now characterize the different phase boundaries starting from the  $\beta$  phase which is stable at normal pressure and ambient temperature.

#### B. Order-disorder transition between the $\alpha$ and $\beta$ phases (below 0.477 GPa)

The position of the transition from the ordered, low-conductivity state to the disordered high-conductivity state has been determined by electrical conductivity measurements in two previous studies.<sup>5,7</sup> In the first of these<sup>5</sup> the transition temperature is given for only two pressures, and in the second study the transition temperature at normal pressure is found to be 323.5 K, which is slightly low and might be an indication that the sample could have been nonstoichiometric.<sup>19,22</sup> In any case, they report a

considerable error range for the transition temperatures and a larger slope,  $dT/dp$ , near normal pressure than at higher pressures (see Fig. 5 on p. 1413 of Ref. 7).

Within experimental error our transition temperatures increase linearly from 325 K at normal pressure up to 333 K at 0.36 GPa. After passing a maximum of 334 K at about 0.42 GPa, the transition temperature approaches the triple point in an abnormal way. For the linear section this investigation gives a slope  $dT/dp$  of 22 K/GPa while our previous study gave 26 K/GPa (Ref. 10) for a sample that had been prepared by precipitation and thus contained a slight amount of  $\beta\text{-AgI}$  as impurity. Our slopes are considerably smaller than those of the two previous investigations, 61 K/GPa (Ref. 5) and 71 K/GPa (Ref. 7), respectively.

In our previous study of a precipitated sample<sup>13</sup> DSC gave an additional small peak at a slightly lower temperature. Two DSC peaks are characteristic for samples that contain a slight excess of either AgI or  $\text{HgI}_2$ , which is soluble in  $\alpha\text{-Ag}_2\text{HgI}_4$  but not in  $\beta\text{-Ag}_2\text{HgI}_4$  (Refs. 15 and 22). However, the small peak was only present when the pressure was below 0.4 GPa (Ref. 13), which is somewhat higher than the pressure, 0.3 GPa, for which there is a transformation in pure AgI from  $\beta\text{-AgI}$  to a high-pressure fcc phase with rocksalt structure.<sup>23</sup> (This transition has hysteresis of the order of 0.08 GPa, if the pressure is changed rapidly.<sup>16</sup>) Since the precipitated samples showed only one peak for the order-disorder transition in the range above 0.4 GPa, it appears that the high-pressure fcc AgI is either soluble in both  $\alpha\text{-Ag}_2\text{HgI}_4$  and  $\beta\text{-Ag}_2\text{HgI}_4$ , or insoluble in both. This question will be discussed in more detail below (Sec. III I).

The course of the transition enthalpy is shown in Fig. 2. It is 8.5 kJ/mol at normal pressure while it is approximately constant, 6.2 kJ/mol, from 0.1 GPa up to 0.477 GPa. At normal pressure the volume increase at the order-disorder transition,  $\Delta V$ , is  $0.56 \text{ cm}^3/\text{mol}$  according to a Clausius-Clapeyron calculation for our present study, which is in reasonable agreement with our previous result  $0.65 \text{ cm}^3/\text{mol}$  (Ref. 13). The volume increase is approxi-

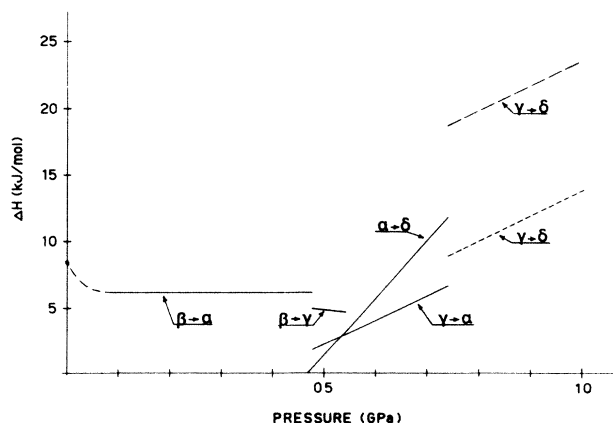


FIG. 2. Measured transition enthalpies ( $\Delta H$ , kJ/mol) for phase transitions. Concerning the transition between the  $\gamma$  and  $\delta$  phases, the long-dashed line is calculated from the conditions at the triple point, while the short-dashed line is measured by increasing the pressure at constant temperature, cf. Fig. 1.

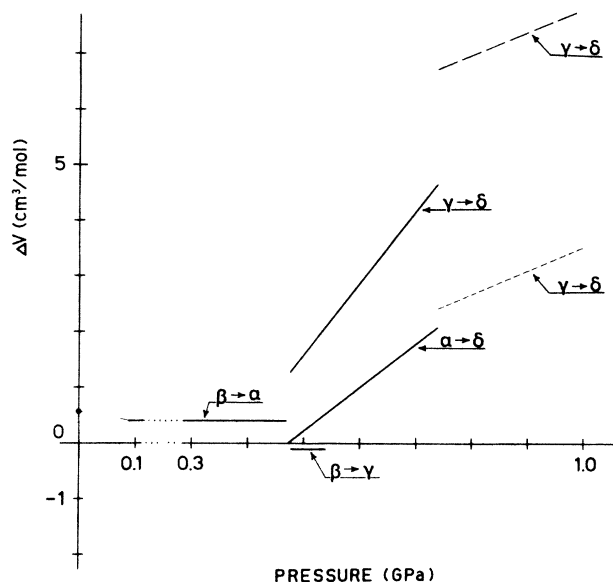


FIG. 3. Volume change ( $\Delta V$ ,  $\text{cm}^3/\text{mol}$ ) calculated according to the Clausius-Clapeyron relation. Two alternatives are considered for the transition between the  $\gamma$  and  $\delta$  phases, see captions of Figs. 1 and 2.

mately  $0.4 \text{ cm}^3/\text{mol}$  over the whole range from 0.001 GPa to 0.42 GPa. Our quoted volume change of  $0.56 \text{ cm}^3/\text{mol}$  at normal pressure can be compared with some results of other studies. Thus, x-ray determinations of the change in lattice constant give  $1.27 \text{ cm}^3/\text{mol}$  (Ref. 5) and a dilatometric study<sup>24</sup> gives  $0.4 \text{ cm}^3/\text{mol}$ .

All the results discussed above concerning the  $\beta\text{-}\alpha$  transition are for heating at constant pressure. Many recordings of transition temperature and enthalpy were also taken for cooling from the  $\alpha$  to the  $\beta$  phase. Over the whole pressure range the transition occurs about 2 K lower for cooling than for heating. At normal pressure that transition enthalpy measured for cooling,  $\Delta H(\alpha\beta)$ , is about 95% of what was obtained for heating,  $\Delta H(\beta\alpha)$ . This ratio decreases when the pressure is increased, and for the range 0.001 to 0.477 GPa we have  $\Delta H(\alpha\beta) \approx 0.8H(\beta\alpha)$ . If the sample is reheated after some time has elapsed the earlier result for  $\Delta H(\beta\alpha)$  is reproduced. Thus, upon cooling, most of the ordering occurs rapidly, but this process does not go to completion at once, and the last fraction orders too slowly to be registered by the DSC plot. In our study of precipitated samples we found a much larger hysteresis, between 5 and 17 K (Ref. 13), which, however, tended to decrease when the sample was cycled many times. These observations for cooling indicate large differences in the kinetics between the stoichiometric and nonstoichiometric salt. A further study of this problem would require a controlled cooling rate, which is not possible with our present device.

### C. Transition from the $\beta$ to the $\gamma$ phase (increasing pressure)

Characteristic for the  $\beta\text{-}\gamma$  transition is the pronounced difference depending on whether the pressure is

increased or decreased. The hysteresis is of the order of 0.13 to 0.16 GPa. This section concerns transitions from the  $\beta$  to the  $\gamma$  phase, solid line in Fig. 1, while the next section covers experiments where the pressure is decreased at nearly constant temperature, i.e., the dotted-dashed line.

It is difficult to determine the phase boundary accurately for pressures slightly above the triple point. Thus, when using the normal procedure of increasing the temperature at constant pressure, it can be difficult to separate the transition from the  $\beta$  to the  $\gamma$  phase from the adjacent  $\gamma \rightarrow \alpha$  transition and, as discussed below, complications also occur if the pressure is changed rapidly at temperatures close to 328 K. As shown in Fig. 1, the phase boundary is nearly horizontal from the triple point up to about 0.54 GPa with the slope  $dT/dp = -7$  K/GPa. Also, the transition enthalpy decreases slightly (Table I), and the decrease in volume is small, of the order of  $-0.1$  cm<sup>3</sup>/mol.

In the region from 0.54 GPa, 328 K to 0.61 GPa, 311 K the transition enthalpy decreases rapidly from about 4.7 to 0.4 kJ/mol, and the phase boundary is strongly curved. Above 0.61 GPa the transition line becomes nearly vertical and it can hardly be located by changing the temperature at constant pressure. Thus, the  $\beta \rightarrow \gamma$  transition could only be studied by isothermal increases of the pressure. With the available equipment we could follow the transition only down to 278 K, where it occurred at 0.64 GPa. The slope is thus  $dT/dp \approx -1.1 \times 10^3$  K/GPa for the region from 311 to 278 K.

As is reported in Secs. III E and III G below, other experiments where the pressure is increased at nearly constant temperature tend to shift the phase transition ( $\alpha$  to  $\gamma$  in Sec. III E, and  $\delta$  to  $\gamma$  in Sec. III G) toward higher pressures. In those two cases we are dealing with disorder-order transitions, while in the  $\beta\gamma$  case we have a transition between two ordered phases. Thus there is a difference between this section and the two other ones (III E and III G) concerning the type of transition. It

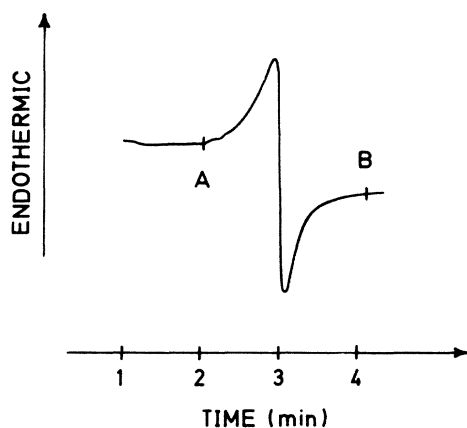


FIG. 4. Transition from the  $\beta$  to the  $\gamma$  phase followed immediately by a transition back to the  $\beta$  phase. The temperature was kept constant, 328 K, while the pressure was increased with the rate  $dp/dt = 25$  MPa/min. The event started near 0.56 GPa.

might well be that the real equilibrium line is located at a slightly lower pressure than indicated by the solid line in Fig. 1. At this nearly vertical phase boundary the transition enthalpy was found to decrease by more than an order of magnitude when the temperature is reduced 33 K; consequently the volume change  $\Delta V$  does the same, cf. Table I. This means that the phase boundary gradually becomes a vertical line, and it should end either in a critical or a triple point.

A scan along a line that is nearly parallel with a phase boundary can under certain conditions (involving the reaction kinetics as well as the scanning rate) give rise to a situation where a transition is followed immediately by its reversal. We have studied this in some detail by performing pressure scans in the vicinity of the nearly horizontal  $\beta\gamma$  boundary (0.477 to 0.54 GPa) discussed above. An example of a  $\beta \rightarrow \gamma \rightarrow \beta$  transition is shown in Fig. 4. In this case the pressure was increased with a rate of about 25 MPa/min at a temperature of 328 K. The event started when the pressure had reached about 0.56 GPa, and it was over in two minutes. The behavior is a feedback effect due to the local temperature changes caused by rapid enthalpy changes. Thus, the rapid endothermic transition from the  $\beta$  to the  $\gamma$  phase cools the sample well below the transition point, and this triggers the exothermic transition from the  $\gamma$  to the  $\beta$  phase. (The instantaneous temperature drop in the sample can be estimated to be of the order of 25 K, if the endothermic transition is very rapid.) The performance of such an experiment can be varied within certain limits, and this affects the details of the DSC trace. To our knowledge this type of transition reversal has not been observed before. Very special conditions must be fulfilled for its occurrence, but we refrain at present from a more-detailed discussion, since it is of limited interest for a presentation of the phase diagram of the system we are studying.

#### D. Transitions from the $\gamma$ to the $\beta$ phase (decreasing pressure)

An unexpected effect is observed when going back from the  $\gamma$  to the  $\beta$  phase by lowering the pressure. Thus in the whole temperature range from slightly below the horizontal line, about 328 K down to 278 K (which was the lowest temperature that could be achieved with our present equipment), the  $\gamma \rightarrow \beta$  transition occurs at around 0.465 GPa with a very small scatter of about  $\pm 4$  MPa, marked with a dotted-dashed line in Fig. 1. It is remarkable that this transition pressure is hardly influenced by the temperature, in contrast to the  $\beta \rightarrow \gamma$  transition discussed above.

As is shown in Table I and Fig. 5, both the latent heat (absolute value of the transition enthalpy) and its temperature gradient  $dH/dT$  are larger for the  $\gamma \rightarrow \beta$  transition (reduced pressure) than for the  $\beta \rightarrow \gamma$  one (increased pressure). The ratio  $\Delta H(\gamma\beta)/\Delta H(\beta\gamma)$  decreases from 2.4 to 1.6 in the studied temperature range, and for both expressions  $\Delta H$  approaches zero at about 270 K. Thus, the experiments with decreasing pressure also support the conclusion in Sec. III C that there should be either a critical or a triple point some 10 K below the lowest temperature

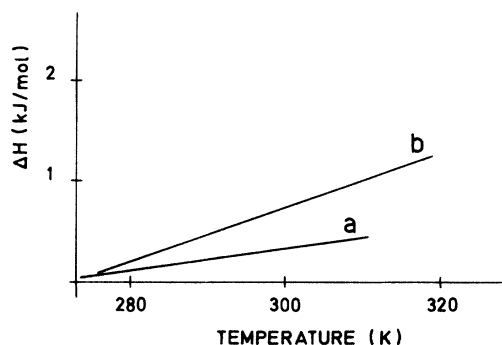


FIG. 5. Transition enthalpy for  $\beta \rightarrow \gamma$  phases. Line *a* corresponds to increasing pressure (0.61 to 0.64 GPa), while line *b* is obtained for decreasing pressure (approximately 0.465 GPa). Thus line *a* is endothermic while line *b* is exothermic.

that could be achieved.

It might be recalled in this connection that we have found recently that metastable mixtures of the  $\beta$  phase and some high-pressure phases can exist for a long time at normal pressure and temperatures near room temperature.<sup>14</sup> This was found also for stoichiometric samples prepared by the solid-state reaction, i.e., for the same type of samples as used in the present investigation. So far, this has been done under reproducible conditions only for hydrostatic pressure of at least 2 GPa, i.e., above a transition found by Kamigaki *et al.*<sup>9</sup> Work is in progress to establish whether it is the  $\gamma$  phase or some other high-pressure phase that can exist as a metastable "impurity" at normal pressure.

#### E. Order-disorder transition between the $\gamma$ and $\alpha$ phases (0.477–0.74 GPa)

In the phase diagram, Fig. 1, the presumably ordered  $\gamma$  phase is separated from the disordered  $\alpha$  phase by a straight line between the triple points 0.477 GPa, 328.5 K and 0.74 GPa, 400.5 K. The given position of the phase boundary is taken from experiments where the temperature was increased at constant pressure. We also studied the  $\gamma \rightarrow \alpha$  transition by reducing the pressure at constant temperature, and the agreement was good with the results of the isobaric determination. The reverse transition was followed in two different ways. Thus, if the pressure was increased at constant temperature, the  $\alpha \rightarrow \gamma$  transition occurred at much higher pressures than the indicated line. The difference could exceed 0.1 GPa. For cooling at constant pressure, the hysteresis of the  $\alpha \rightarrow \gamma$  transition was between 10° and 20°. It is obvious that the reproducibility is better when going from an ordered to a disordered phase than for the opposite transition. There is thus a similarity in this aspect between the  $\gamma \rightarrow \alpha$  and the  $\beta \rightarrow \alpha$  transitions.

Characteristic of the  $\gamma \rightarrow \alpha$  transition is the large, approximately linear increase of the transition enthalpy over the pressure range of about 0.26 GPa, see Table I and Fig. 2, from 1.28 to 6.77 kJ/mol. An extrapolation (into the region of the  $\beta$  phase) gives  $\Delta H = 0$  and  $\Delta V = 0$  for 0.38 GPa and 303 K. The error quoted for  $\Delta H$  in Table I is

about 25% at the first triple point (0.477 GPa) and 10% at the high triple point (0.74 GPa). This is partly due to the above-mentioned (Sec. III C) difficulty to separate the  $\beta \rightarrow \gamma$  and  $\gamma \rightarrow \alpha$  transitions near the first triple point.

#### F. Transitions between the disordered $\alpha$ and $\delta$ phases (below 0.74 GPa)

The boundary between the  $\alpha$  and  $\delta$  phase extends from about 425 K at normal pressure to the triple point at 0.74 GPa, 400.5 K. One can clearly distinguish two parts separated by a singularity at 0.474 GPa, 382 K. The section from normal pressure to the singularity has a small maximum at about 428 K, 0.045 GPa, while the section between the singularity and triple point is a straight line with a slope  $dT/dp = 69$  K/GPa. Let us first of all focus our attention on this latter line. A remarkably rapid change of the transition enthalpy is found. Over a pressure range of 0.26 GPa it increases from zero at the singularity to 11.9 kJ/mol at the triple point, see Table I and Fig. 2. Since the slope is constant, one can conclude that at the singularity point a negligible volume change accompanies the transition from the  $\delta$  to the  $\alpha$  phase. Two alternatives are possible here: either we face a critical point or the phase transition changes its character. Of these alternatives the second one is valid. Namely, that in a wide range below the singularity at least down to 0.156 GPa, a second-order transition takes place, being characterized mainly by a discontinuity in the heat capacity. We traced the phase transition on both sides of the singular point by small changes of pressure, finding clearly that we encounter here not a minimum but a singular point—that is, an intersection of two straight lines. The very nature of the transitions around the singularity is shown in Fig. 6. This figure presents a sequence of four transitions observed in the pressure range of about 10 MPa only, from

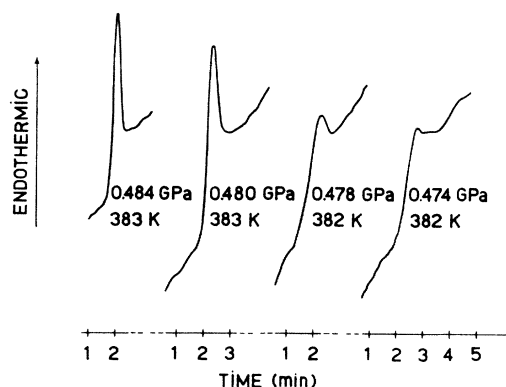


FIG. 6. DSC traces for the endothermic transition from the  $\alpha$  to the  $\delta$  phase at four different pressures. In each case the heating rate  $dT/dt$  was 3.3 K/min. The quoted transition temperatures are rise temperatures. For the highest pressure, 0.484 GPa, the curve shows not only a transition enthalpy,  $\Delta H$ , which is characteristic of a first-order transition, but there is also a distinct change in the heat capacity,  $\Delta c$ , characteristic of a second-order transition. The latter dominates completely for the lowest pressure, 0.474 GPa. When comparing the whole sequence from 0.484 to 0.474, the drastic drop in  $\Delta H$  is most striking, but it is also evident that  $\Delta c$  is increased.

0.484 GPa to 0.474 GPa, and of slightly more than one degree. It is important to notice that the transition at 0.484 GPa and 383 K shows not only a pronounced transition enthalpy,  $\Delta H$ , but there is also clear evidence of an abrupt change,  $\Delta c$ , of the heat capacity. Thus, there are both first- and second-order contributions to the transition. When going to lower pressures the rapid drop in  $\Delta H$  is the most striking phenomenon, but there is also an increase of the heat-capacity jump  $\Delta c$ . At 0.474 GPa and 382 K the enthalpy peak is negligible. In fact we are very close to the singular point in the phase diagram. Decreasing the pressure further one notices only heat-capacity discontinuities at increasing temperatures. This trend is followed down to about 0.156 GPa, below which again enthalpy peaks become evident, but of more complex nature. It seems that here a new phase boundary intersects, coming down from higher temperatures. But as is known from normal pressure behavior,<sup>21</sup> a partial decomposition of silver mercury iodide probably takes place; therefore we limit ourselves to indicating the temperature as function of pressure only for the first transition observed. A complete analysis would require an extension to higher temperatures. Of course this necessitates an analysis of possible composition changes, which is equivalent to switching over to, at least, a two-component system. We think that other experimental methods—for instance, an x-ray analysis—must then also be considered, and that the DSC characteristic alone seems not to be very informative in this case.

Concerning the singularity at 0.474 GPa, 382 K, there is obviously reason to expect that it could instead be a triple point. We have searched in vain for any indication of this. We have thus made many scans with increasing as well as decreasing pressure, but we have not obtained any indication at all of any transition enthalpy near 0.47 GPa anywhere in the range from 382 K down to 328 K. The possibility remains that there is a transition with  $\Delta H = 0$  corresponding to a vertical line. Such a transition might be detectable by studying, e.g., the pressure dependence of the electrical conductivity. However, if such a vertical line exists, it would mean that there is a quadruple point at 328 K instead of the triple point, and such an alternative does not seem very likely, cf. Sec. III H.

For normal pressure the transition enthalpy is 11.5 kJ/mol at 425 K. This is in good agreement with the less accurate estimate by Otsubo *et al.*<sup>21</sup> from their DTA curves (12.6 kJ/mol).

#### G. High-pressure order-disorder transition between the $\gamma$ and $\delta$ phases (above 0.74 GPa)

The first part of this phase boundary was obtained from the obvious requirement in the vicinity of a triple point that the sum of the transition enthalpies, as well as of the volume changes, for all involved transitions has to be zero. From the known  $\Delta H$  and  $\Delta V$  of the  $\alpha \rightarrow \delta$  and  $\gamma \rightarrow \alpha$  transitions, see Table I, we obtained the long-dashed line shown in Fig. 1 for the  $\gamma\delta$  phase boundary. It is, as expected, located between the extensions of the  $\alpha\delta$  and  $\gamma\alpha$  lines. We also studied the  $\delta \rightarrow \gamma$  transition by increasing the pressure at nearly constant temperature. This was

done in the range 0.8 to 1.0 GPa, and the dotted line of Fig. 1 was obtained. This line lies below the calculated one, but this can be understood, since an isothermal pressure increase usually leads to a higher transition pressure rather than one corresponding to the results of isobaric heating. We therefore think that the calculated phase boundary represents equilibrium conditions better than the experimental one.

The above-mentioned scans with increasing pressure at (nearly) constant temperature resulted in (exothermal) transition enthalpies which correspond to the short-dashed line in Fig. 2 (latent heats, i.e., endothermal enthalpies shown). According to these measurements the latent heat is pressure dependent with  $d(\Delta H)/dp > 0$ . However, in the vicinity of the triple point, the experimental result is only about half of the mentioned calculated transition enthalpy. This indicates that the transition from the disordered  $\delta$  to the ordered  $\gamma$  phase is very sluggish and that it in part is so slow that it is not registered by the DSC instrument. As an indication of what the true transition enthalpy might be, we have displaced the experimental line upwards to the enthalpy in the vicinity of the triple point. It is of course quite possible that the true line has another slope than the one chosen by us for the long-dashed line in Fig. 2.

#### H. Comment on properties in the vicinity of 0.46 GPa

After our description of the phase diagram for pressures up to 1 GPa and temperatures up to slightly above the transition to the  $\delta$  phase, let us point out an additional interesting property, namely that the singular point for the  $\alpha \rightarrow \delta$  transition, the  $\alpha, \beta, \gamma$  triple point, and the  $\gamma \rightarrow \beta$  transition for decreasing pressure, dashed-dotted line in Fig. 1, are all occurring at nearly the same pressure of about 0.46 GPa. It is hardly to be expected that just by chance this pressure is the same for these three characteristic features of the phase diagram, especially when taking into account that this constancy is valid over a temperature range of more than 100 K.

#### I. Influence of impurities

Contrary to some previous studies,<sup>5,6,9,11</sup> we did not observe any phase transition at room temperature around 0.4 GPa when the pressure was increased. A probable explanation of this discrepancy is that the quoted investigators prepared their  $\text{Ag}_2\text{HgI}_4$  by precipitation, and according to our recent observations,<sup>19</sup> it is likely to expect that their samples were slightly nonstoichiometric and contained a slight amount of AgI as impurity. For such samples the DSC trace of the  $\beta \rightarrow \alpha$  order-disorder transition exhibits an additional small peak which disappears around 0.4 GPa (Ref. 13). This can be explained by considering the phase diagram of pure silver iodide,<sup>23</sup> which has a phase transition above 0.3 GPa where  $\beta\text{-AgI}$  and  $\gamma\text{-AgI}$  both go over to a fcc phase. If this fcc phase is more soluble in  $\beta\text{-Ag}_2\text{HgI}_4$  than  $\beta\text{-AgI}$  is, it would cause the mentioned disappearance of the small peak. (There would be only one peak for the order-disorder transition also if fcc AgI is insoluble in both the ordered and the disordered phase of  $\text{Ag}_2\text{HgI}_4$ .)



It is of interest in this context that a maximum of the electrical conductivity was taken as a criterion of a phase transition.<sup>5,6</sup> It is difficult to say how much the suggested small amount of impurity AgI could have contributed to the previously obtained conductivities, but it might be of interest to compare with the pressure dependence of pure silver iodide.<sup>23,25-30</sup> Thus for constant temperature the conductivity of AgI increases when the pressure is raised; there is a sudden increase at the phase transition, followed by a conductivity decrease in the fcc phase. A further discussion must await a study of the pressure dependence of the conductivity of stoichiometric  $\text{Ag}_2\text{HgI}_4$  prepared by a solid-state reaction.

#### J. Comparison with other studies and final conclusions

The phase transition around 0.6 GPa, observed by all previous investigators by the electrical resistance method as well as by Raman spectroscopy coincides roughly with the  $\beta \rightarrow \gamma$  or  $\alpha \rightarrow \gamma$  transitions of our phase diagram, Fig. 1. It is this transition from the ordered ( $\beta$ ) or disordered ( $\alpha$ ) normal pressure phases to the ordered  $\gamma$  phase, prob-

ably a fcc phase, which causes practically no controversy. It seems obvious that the techniques applied previously<sup>5-11</sup> (electrical conductivity and Raman spectroscopy) were not suitable for establishing all phase boundary lines involved. Either the changes of the studied property were not large enough to be detectable at some phase transitions, or the involved pressure changes were too large and not always purely hydrostatic. It is an advantage of the DSC technique that the phase transitions can be followed under well-defined hydrostatic conditions by determining both the temperatures and the enthalpy changes in the same measurement. We think that the phase diagram presented can serve as a solid basis for the investigation of different properties of stoichiometric silver mercury iodide in the indicated temperature and pressure range.

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