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Transition enthalpies of silver iodide in the high-pressure region determined by differential scanning calorimetry

B.-E. Mellander, B. Baranowski,* and A. Lundén
Department of Physics, Chalmers University of Technology, S-412 96 Göteborg, Sweden
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Differential scanning calorimetry was used at high pressure to determine the transition enthalpies for five solid-solid phase transformations in AgI. The maximum pressure was 7.4 kbars. The very sluggish transitions to the intermediate phase were investigated using both β- and γ-type AgI as the starting material. No differences in transition pressure for the two types could, however, be detected.

I. INTRODUCTION

The choice of a calorimetric method suitable for high-pressure conditions is difficult since the limited available working volume in the high-pressure cell as well as the high heat capacity and conductivity of the pressure-transmitting medium have to be taken into account. With few exceptions[1-3] all data of the transition enthalpy under high pressure were either calculated from Clausius-Clapeyron's equation or determined by differential thermal analysis.

In order to get a direct measure of the heat effects and therefore a better accuracy, differential scanning calorimetry (DSC) has been used in this investigation. The only previous DSC measurements at high pressure known to the authors[1-3] were performed for pressures up to 2.5 kbars (0.25 GPa). Our present DSC measurements have been done to determine the transition enthalpies for five solid-solid transitions in AgI for pressures up to 7.4 kbars. The phase diagram of AgI contains an intermediate phase which has caused much controversy since its discovery by Van Valkenburg[4] in 1964. Our recent redetermination of the phase diagram[5] using electrical-conductivity measurements showed the extreme sluggishness of the transitions to this phase.

At normal temperature and pressure AgI exists in two modifications: the β phase (wurtzite structure) and the γ phase (sphalerite structure), where the latter is claimed to be metastable.[6] Our earlier work[5] dealt only with γ-type material, and, in order to detect if there were any differences between β- or γ-phase material concerning the transitions to the intermediate phase, both were used in the present investigation. Furthermore, enthalpy measurements make it possible to calculate dp/dT for the phase-transition lines if the density change is known.

II. EXPERIMENTAL

Differential scanning calorimetry implies that during heating (or cooling) the temperature difference between the sample and a reference material is kept equal to zero by additional heating of either of them. The additional power needed to keep the temperatures equal is recorded. A phase transition is detected as a peak, and the transition enthalpy can be calculated from the area under the peak.

In the present work commercial DSC equipment (Rigaku, Japan) was converted for use at high pressure. The DSC measuring head was placed inside the externally heated pressure cell of a two-step high-pressure apparatus (Basset-Bretagne-Loire, France) using argon as the pressure-transmitting medium. The sample and the reference were placed in platinum capsules closed by platinum lids. The amount of sample was less than 40 mg. The reference capsule contained aluminum oxide.

The silver iodide used was stated to be 99.9% pure (Riedel-Dehaën, Hanover, Germany) and x-ray investigations showed that it was dominantly of the β type. It was used in this form for most experiments, but since γ-phase material was needed for some experiments, this was prepared from the β-type material by pressing in a pellet die at approximately 2 kbars. In this case the x-ray diffractograms showed the characteristic pattern of the γ phase.

The main requirement for an acceptable run is to avoid any convection around the measuring head of the high-pressure-transmitting gas. Its large heat capacity would cause a large perturbation for the sensitive scanning device. To avoid convection, all free space was filled with high-temperature-resistive ceramic fiber. Our high-pressure apparatus allowed DSC measurements not only by scanning the temperature but also by scanning the pressure, which made it possible to investigate transitions where the phase lines are very steep.

A stable basis line is important for an accurate evaluation of the heat effect. At about 1 kbar strong convection made measurements difficult, but at higher pressures the base line was again

very stable. In fact it was even comparable to that at normal-pressure conditions. To calibrate the measurement of enthalpies, the peak area obtained at the melting of indium (99.999% pure, Rigaku, Japan) was measured as a function of pressure. The calibration was made under the assumption that the enthalpy of melting of indium is independent of pressure in the pressure range investigated.

For the constant-pressure measurements the standard deviation of the mean of the enthalpy data is normally less than 2%. It is difficult to estimate the contributions from possible systematic errors. In all cases the total error is better than ±5%. The constant-temperature measurements are used here to determine small values of enthalpy, and it is difficult to control the rate of pressure change. Thus the total error might in this case be as large as ±10%.

The temperature was measured by Platinel II thermocouples placed under the sample and reference cups. To check the temperature measurement and the effect of pressure on the emf of these thermocouples, the melting temperatures of indium were compared to literature data.[7] According to these measurements the pressure dependence is small and no corrections were made for this effect. The error in the temperature measurements is with few exceptions less than ±2 K. The pressure was measured by a manganine gauge with an accuracy of 1%.

TABLE I. Measured enthalpies for transitions to the α phase compared to calculations by Bridgman (Ref. 8).

Transformation	Pressure (kbars)	ΔH DSC (kJ/mole)	ΔH calculated (Ref. 8) (kJ/mole)
$\beta\gamma \rightleftharpoons \alpha$	0.001	6.06	5.66
	1.0		5.68
	2.0	5.15	5.14
	2.6	4.78	
	2.9		4.76
fcc $\rightleftharpoons \alpha$	2.9		4.16
	3.4	3.94	
	3.9		4.09
	4.9		3.72
	5.0	3.70	
	5.9		3.08
	6.0	3.01	
	6.4		2.74
	7.4	2.25	

III. RESULTS AND DISCUSSION

The results for the five transitions in AgI which are within the temperature and pressure range of the present equipment are summarized in Tables I–III. The phase diagram is shown in Fig. 1. Tables I and II also present enthalpies calculated from the Clausius-Clapeyron equation

$$dp/dT = \Delta H/T\Delta V$$

where ΔH is the transition enthalpy. ΔV, the volume change at the phase transition is taken from the literature,[8,9] T is the absolute temperature, and dp/dT is the slope of the phase line in the phase diagram. It should be pointed out here that the uncertainty of these calculations can be considerable, especially due to the uncertainty in the determination of the slope of the phase lines.

a. The $\beta/\gamma \rightleftharpoons \alpha$ transition. Our transition enthalpy at normal pressure is in good agreement with that of Nölting and Rein,[10] 6.15 ± 0.29 kJ/mole. At high pressures Bridgman's[8] calculated enthalpies agree well with the present results, and the position of the phase line is in good agreement with earlier investigations.[8,11-13]

b. The fcc $\rightleftharpoons \alpha$ *transition.* The enthalpies we obtained are in good agreement with Bridgman's calculated ones and the transition temperatures fitted well with those of our previous study.[5] An example of the DSC peak at 5.0 kbars is shown in Fig. 2.

c. The $\beta/\gamma \rightleftharpoons$ fcc *transition.* The phase line of this transition is steep. In some earlier papers[9,14] it has even been said to be parallel to the temperature axis, which would mean that the transition enthalpy is equal to zero. Because of the steep slope our DSC measurements were done as pressure scans. This and the low values of the enthalpy of transformation caused a lower accuracy of the enthalpy measurement for this transition than for the ones mentioned above. Table

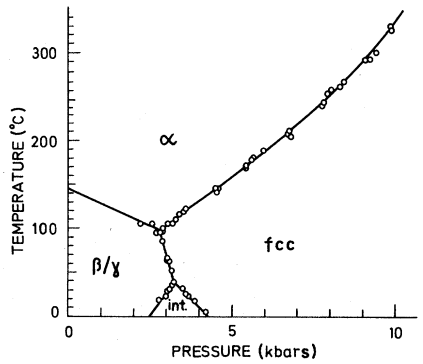

FIG. 1. The phase diagram of AgI according to Ref. 5.

TABLE II. Measured enthalpies for fcc–β/γ transitions compared to calculations by Bridgman (Ref. 8) as well as with calculated values using ΔV data from Bridgman and dp/dT from the phase diagram in Ref. 5. The absolute values of the enthalpies are given in the table.

Transformation	Temperature (°C)	ΔH DSC (kJ/mole)	ΔH calculated (Ref. 8) (kJ/mole)	ΔH calculated (Refs. 8 and 5) (kJ/mole)
fcc → β/γ	90	0.92	0.68	1.4
	70	0.81	0.55	1.3
	50	0.70	0.46	1.2

II presents the results for runs at decreasing pressure. Due to the necessary high scanning rate this transition showed a clear hysteresis. With increasing pressure the transition started about 0.3-kbars higher pressure than predicted by the phase diagram (Fig. 1). With decreasing pressure the phase transition was delayed about 0.5 kbars. With increasing pressure the transition is endothermic, which shows that dp/dT for the phase line is negative since ΔV is negative.[8] Calculated values of transition enthalpy are strongly affected by dp/dT, and the apparent deviations are thus within the expected range.

d. The β/γ ⇄ intermediate ⇄ fcc transitions. The measurements were also in this case made as pressure scans. The transitions to the intermediate phase are very sluggish and influenced by hysteresis.[5] In the present work both β- and γ-AgI were used to determine if the transition pressure is dependent on the structure of the starting material. However, no such differences could be detected. The first time a β or γ sample was pressurized the transition β/γ → int. did not appear until at about 3.6 kbars at 21 °C (delayed 0.7 kbars). When a sample that had been in the intermediate phase before was pressurized a second time the transition occurred earlier, and the delay was now only about 0.2 kbars. This "memory effect" has been observed before in optical observations[14] and electrical-conductivity measurements.[5] If the pressure were reduced again after the sample had been transformed to the intermediate phase, the transition int. → β/γ occurred according to the phase diagram.

The transition int. → fcc started at about the expected pressure, but when the pressure was lowered the fcc → int. transition was delayed 1.5–2.0 kbars and was so closely followed by the int. → β/γ transition that even they were difficult to separate. Figure 3 shows the DSC peaks for the transitions β/γ → int. → fcc at 21 °C for a sample that has previously been in the intermediate phase.

In our earlier paper[5] it was shown that, if the first run took several days, the transition γ → intermediate would start at a lower pressure than for the usual rates, and it was suggested that the transition might not appear at all in a fast run. The present work shows that the transition takes place even when the scanning speed is rather high, but, e.g., at 21 °C the β/γ → intermediate transition starts at a pressure only about 0.2 kbars lower than the int. → fcc transition.

The DSC measurement simplifies the separation of the β/γ → int. and int. → fcc transitions since the first is exothermic and the second is endothermic. Using other methods of detection these two transitions could easily be interpreted as being only one for a first run. Using the ΔV values of Hinze[9] and the present transition enthalpies the slope of the phase lines can be calculated and compared to the phase diagram[5] published earlier (see Table III).

These calculations show that the β/γ ⇄ int. phase line has a positive slope which, however, is somewhat steeper than in our phase diagram.[5]

TABLE III. Measured transition enthalpies for the intermediate phase. The calculated dp/dT data are obtained from our enthalpy data and the ΔV data of Hinze (Ref. 9). dp/dT from the phase diagram in Ref. 5 is given for comparison.

Transformation	Temperature (°C)	ΔH DSC (kJ/mole)	$\frac{dp}{dT}$ calculated (Pa/K)	$\frac{dp}{dT}$ phase diagram (Pa/K)
β/γ → int.	25	−0.43	0.78×10^6	2.0×10^6
int. → fcc	21.5	0.46	-0.31×10^6	-2.8×10^6

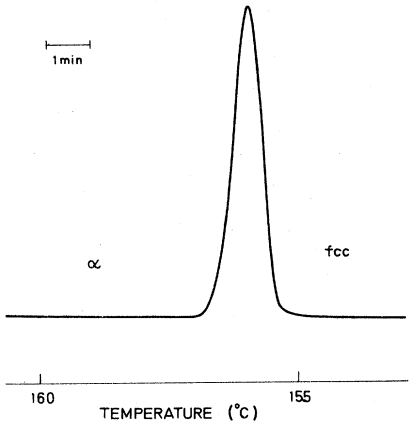

FIG. 2. The DSC peak for the $\alpha \rightarrow$ fcc transition in AgI at 5.0 kbars.

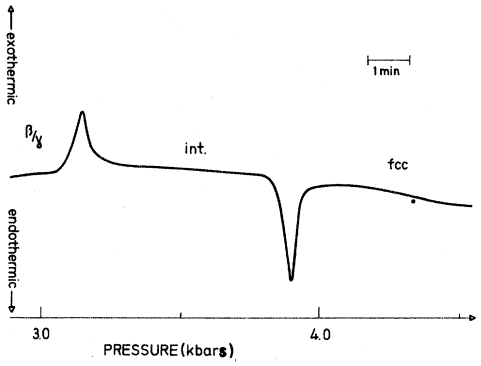

FIG. 3. The DSC peaks for the $\beta/\gamma \rightarrow$ int. $\rightarrow$ fcc transitions in AgI at 21 °C.

The slope of the int. $\rightarrow$ fcc phase line is negative, and the calculated value indicates a much steeper slope of the phase line than reported for the phase diagram. The accuracy of our two calculated slopes is of course dependent on that of Hinze's estimation of the density of the intermediate phase. To determine the proper positions of the phase lines is difficult for these sluggish transitions, and the phase lines in our previous paper[5] correspond to transitions going from the intermediate phase. It should also be noted that Hanson *et al.*[15] in their Raman-spectrum investigation found that the intermediate phase disappeared at about −70 °C, which would mean that the width of the intermediate phase decreases at lower temperatures. At present we do not have facilities to check this.

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*On leave of absence from the Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland.

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