Phase Diagram of the System Copper(I) Iodide + Cesium Iodide[†]

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The phase equilibrium diagram for the CuI + CsI system has been redetermined by differential scanning calorimetry and X-ray diffraction. The phase diagram exhibits three intermediate compounds—$Cs_3Cu_2I_5$, melting incongruently at 663.0 K, $CsCu_2I_3$, melting congruently at 656.0 K, and $CsCu_9I_{10}$, undergoing a solid-state disproportionation reaction to CuI + $CsCu_2I_3$ at 604.8 K. The existence of $CsCu_9I_{10}$, derived from DSC studies in accordance with the phase rule, is not shown by X-ray diffraction investigations.

Introduction

The first information about phase equilibria in the CuI + CsI system comes from Takahashi et al.,[1] who were searching for new superionic compounds based on copper(I) halides. In the system CuI + CsI no intermediate compound of the $RbAg_4I_5$ type was found. Instead, an incongruently melting compound $CsCu_9I_{10}$ was reported to be stable between 606 K and 621 K.

Two other compounds in the system—$CsCu_2I_3$ and Cs_2CuI_3—were discovered by Jouini et al.,[2,3] and their crystal structures were described. The CuI + CsI phase diagram[3] shows them as compounds melting incongruently at 621 K and 658 K, respectively. The compound $CsCu_9I_{10}$ decomposes in the solid state at 601 K; it is considered as stable at room temperature, although it was not identified on X-ray diffraction patterns.[3]

A new compound $Cs_3Cu_2I_5$ was obtained by Bigalke et al.[4] via crystallization from acetone or acetonitrile solution of CuI and CsI. Since the crystal displays the same lattice constants as Cs_2CuI_3,[3] the latter formula was supposed to be wrong.[4]

In 1993 Yamamoto[5] presented a phase diagram for the CuI + CsI system with two compounds which are stable at room temperature—$Cs_3Cu_2I_5$, melting incongruently at 625 K, and $CsCu_2I_3$, melting congruently at about 630 K (the value taken from the graph)—and a third one—$CsCu_9I_{10}$, existing in the previously reported[1] narrow range of temperature. The composition of the compound was deduced from the position of a rather flat maximum on the conductivity isotherm at 610 K.

We hoped that we would be able to clarify some discrepancies concerning the phase equilibria in the CuI + CsI system and to construct a complete phase equilibrium diagram based on results of thorough studies.

Table 1. Annealing and Quenching Data

series	composition, x_{CsI}	annealing temp/K	annealing time/weeks	quenching
I	0.050	550	16	water
	0.100			
	0.200			
	0.333			
	0.600			
	0.800			
II	0.050	618	6	liquid nitrogen
	0.100			
	0.200			
III	0.050	550	12	liquid nitrogen
	0.100			
	0.200			
	0.500			
	0.667			

Experimental Section

Sample Preparation. CuI (99.999%, Aldrich Chem. Co.) and CsI (99.9%, Aldrich Chem. Co.) were first melted under high vacuum in quartz tubes prior to use.

Mixtures of CuI and CsI for differential scanning calorimetry experiments were prepared directly in silica ampules used for measurements. Their diameter was 6 mm, and their height after sealing under vacuum was between (12 and 14) mm. The bottoms of the ampules were flattened by grinding. An empty ampule sealed under vacuum was used as reference.

Appropriate quantities of CuI and CsI were weighed on a Mettler Toledo AT 261 balance (±0.01 mg). The total mass of a mixture was between (10 and 100) mg. About 70 samples were prepared. Succeeding compositions of samples differed by (2 to 3) mol % or less. The samples were heated in an electric furnace for 2 h at 950 K to obtain a homogeneous liquid, and they were then cooled slowly to room temperature.

Mixtures of CuI and CsI for X-ray diffraction measurements were prepared in silica ampules sealed under vacuum. They were heated to melting and then cooled and kept for several weeks at appropriate temperatures. After annealing, the samples were quenched with water or liquid nitrogen. Details on composition, annealing temperature, and quenching procedure are summarized in Table 1.

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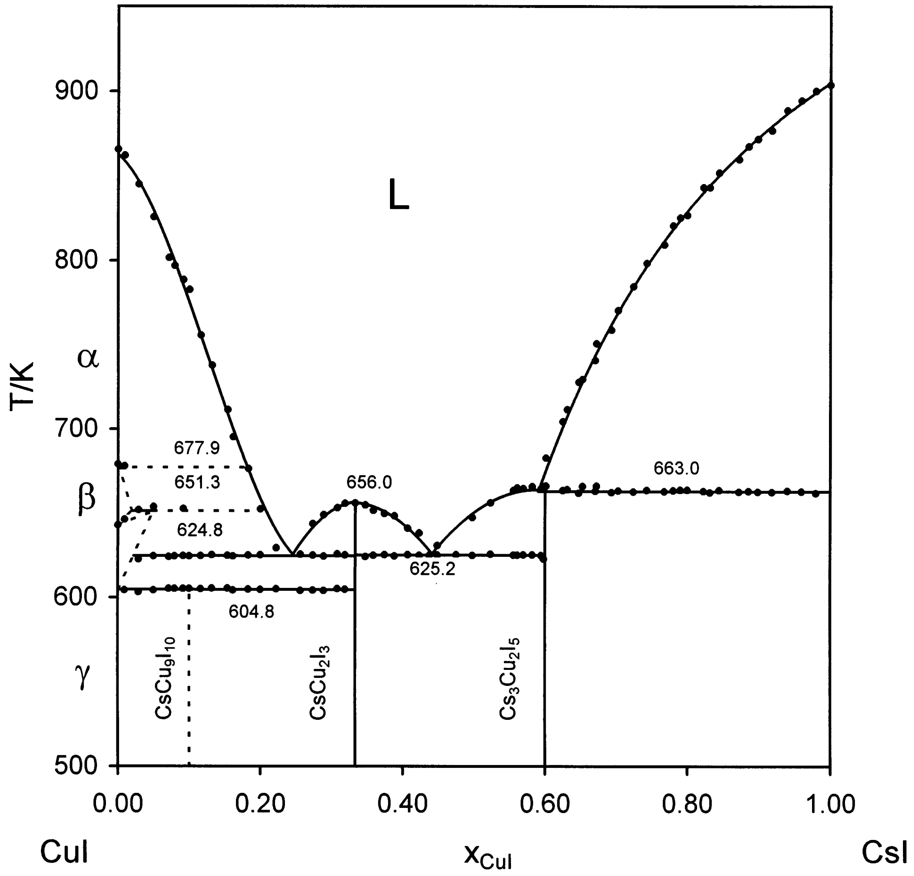

Figure 1. Phase diagram of the CuI + CsI system.

Differential Scanning Calorimetry. Differential scanning calorimetry experiments were performed on a Mettler Toledo DSC25 module controlled by a TC15 TA interface[6−8] and STAR^e 6.0 software.

Prior to measurements, the calorimeter was calibrated with the melting points of indium, tin, lead, zinc, and aluminum. After some preliminary runs, a heating rate of 5 K·min^{-1} and a temperature range of 525 K to 923 K were chosen for DSC experiments for all the CuI + CsI mixtures. Occasionally, they were supplemented by cooling at a rate of (2, 1, or 0.5) K·min^{-1}. The cooling allowed us to discern small liquidus halts or establish the number of thermal events in the case of ambiguity of heating curves. Also special temperature programs, consisting of a sequence of heating, cooling, and isothermal steps, were created in order to let the samples reach equilibrium.

The accuracies of the temperature and the composition determinations were 1 K and 0.1 mol%, respectively. The compositions of the eutectic and peritectic points were determined by extrapolation (liquidus curves and Tamman triangle methods[9]) with an accuracy of ±0.5 mol %.

X-ray Diffraction. Room-temperature X-ray powder diffraction patterns were taken on a diffractometer DRON 3 type with Co Kα radiation, as soon as possible after the samples had been quenched.

Results and Discussion

The phase equilibrium diagram of the CuI + CsI system determined in this study is presented in Figure 1. Invariant (three-phase) equilibria in the system are listed in Table 2, along with corresponding values of temperatures and phase compositions. X-ray diffraction patterns of pure components and of some CuI + CsI mixtures (Table 1, series I) are shown in Figure 2. Tamman triangles for the four reactions observed are gathered in Figure 3. A few examples of illustrative DSC curves are displayed in Figure 4.

Table 2. Invariant Three-Phase Equilibria in the CuI + CsI System

reaction	T/K	type	phase	composition, x_{CsI}
L + CsI ⟺ $Cs_3Cu_2I_5$	663.0	peritectic	liquid	0.59
			CsI	1.00
			$Cs_3Cu_2I_5$	0.60
L + $Cs_3Cu_2I_5$ ⟺ $CsCu_2I_3$	625.2	eutectic	liquid	0.45
			$Cs_3Cu_2I_5$	0.60
			$CsCu_2I_3$	0.33
L + $CsCu_2I_3$ ⟺ γ-CuI	624.8	eutectic	liquid	0.25
			$CsCu_2I_3$	0.33
			γ−CuI	0
$CsCu_9I_{10}$ ⟺ γ-CuI + $CsCu_2I_3$	604.8	peritectoid	$CsCu_9I_{10}$	0.10
			γ−CuI	0
			$CsCu_2I_3$	0.33
L + (α-CuI) ⟺ (β-CuI)	677.9	peritectic	liquid	0.18
			(α-CuI)	<0.009
			(β-CuI)	<0.009
L + (β-CuI) ⟺ (γ-CuI)	651.3	peritectic	liquid	0.21
			(β-CuI)	<0.02
			(γ-CuI)	≤0.05

The system contains three intermediate compounds—$CsCu_9I_{10}$, $CsCu_2I_3$, and $Cs_3Cu_2I_5$. The X-ray diffraction investigations give evidence only for two intermediate compounds—$CsCu_2I_3$ and $Cs_3Cu_2I_5$ (Figure 2).

The existence of the compound $CsCu_2I_3$, melting congruently, is in agreement with the work of Yamamoto[5] and not with that of Jouini et al.[4] However, the maximum on the liquidus curve we have found, indicating the value of 656.0 K for the melting point of the compound, is about 15 K higher than that given in ref 5.

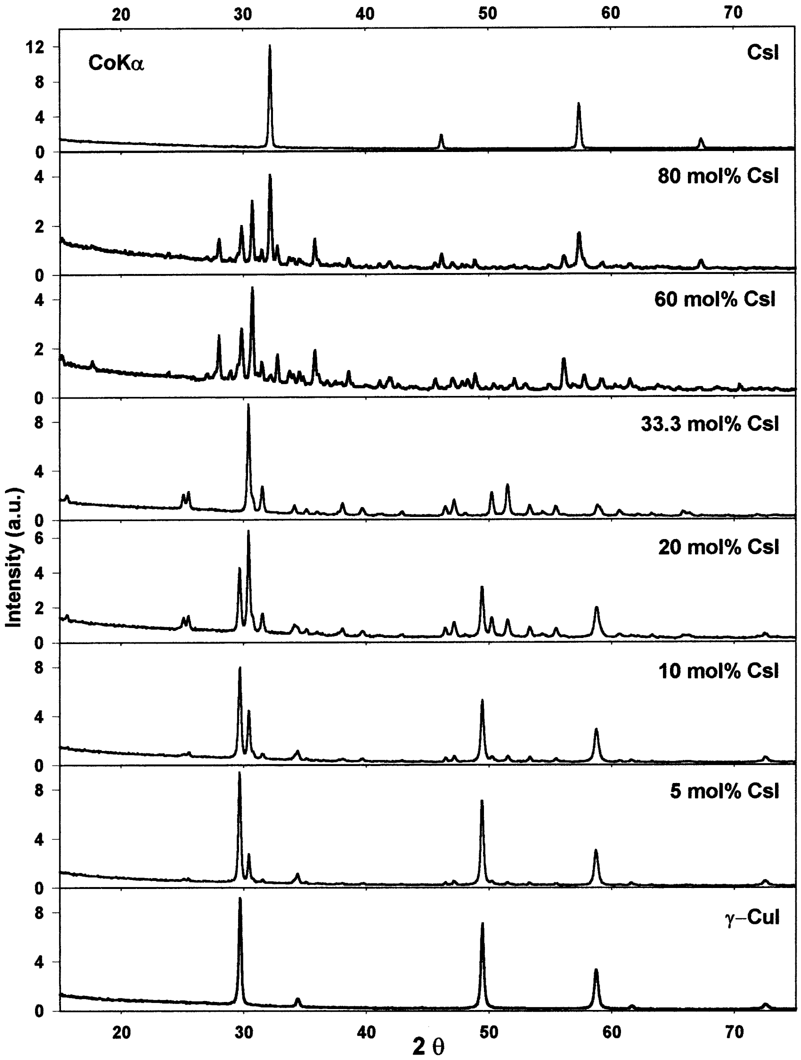

Figure 2. X-ray diffraction patterns of pure components (γ-CuI, CsI) and of CuI + CsI mixtures of series I (Table 1).

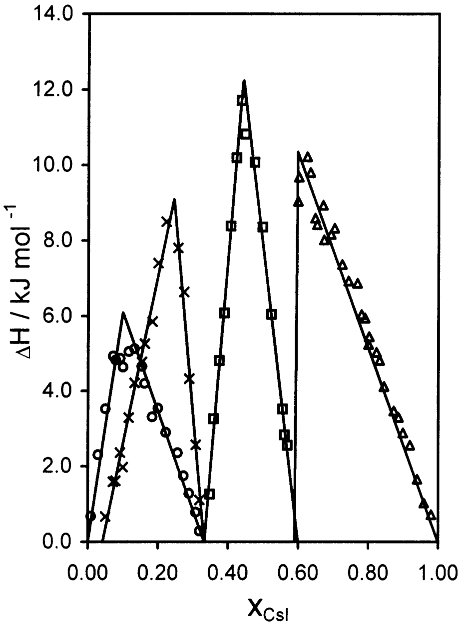

Figure 3. Tamman triangles for some invariant equilibria in the CuI + CsI system: ×, 624.9 K; □, 625.2 K; ○, 604.8 K; △, 663.0 K.

In light of the results derived from both DSC and X-ray diffraction studies, the formula $Cs_3Cu_2I_5$[4,5] and not Cs_2CuI_3[3] was confirmed for a compound appearing near 60 mol % CsI. The compound melts incongruently at 663.0 K, which is 38 K higher than the value given in ref 5. The peritectic point at x_{CsI} = 0.59 lies very closely to that of the composition of the compound (Table 2), and it was difficult to discern if the compound decomposed on melting.

Evidence for the compound to have a composition of 60 mol % CsI and to melt incongruently is as follows: (i) The sample containing 60.0 mol % CsI displayed only an individual $Cs_3Cu_2I_5$ X-ray diffraction pattern (Figure 2) while the samples containing 66.7 mol % CsI (Table 1, series III) and 80.0 mol % CsI (Table 1, series I; Figure 2) reveal CsI lines in addition to those of $Cs_3Cu_2I_5$. (ii) The thermal effect of the reaction occurring at 663.0 K is growing when the bulk composition is changing from nearly pure CsI to x_{CsI} = 0.600; for x_{CsI} < 0.600 the thermal effect falls down rapidly (Figure 3). (iii) Three thermal events are observed on the DSC curve for x_{CsI} = 0.598 (Figure 4)—two corresponding to invariances at 663.0 K and 625.2 K and a weak one, corresponding to the liquidus. (Cooling curves provide a more distinct peak, but due to supercooling phenomena, values of temperature resulting from cooling curves are considered only as tentative ones.)

No intermediate phase was found in the range of composition between 60 and 100 mol % CsI. However, the eutectic reaction at 625.2 K persisted in samples with CsI

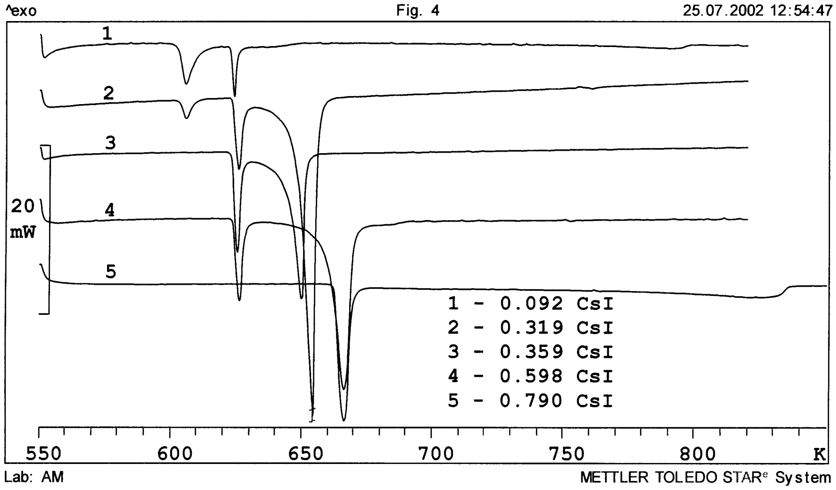

Figure 4. Examples of DSC thermograms performed at a heating rate of 5 K·min^{-1}.

content higher than 60 mol %. The effect seemed to be an additional invariance, but it disappeared when mixtures were annealed in the two-solid region and thus thoroughly equilibrated.

The existence of $CsCu_9I_{10}$[1,3,5] was confirmed by DSC studies. Over the range of composition between nearly pure CuI and $CsCu_2I_3$, all the DSC thermograms revealed an endothermic peak with a sharp onset at 604.8 K (Figure 4). The maximal enthalpy associated with this effect was found at $x_{CsI} = 0.100$, as given by intersection of two sides of the Tamman triangle (Figure 3). Thus, the invariance can be ascribed to the equilibrium of three solid phases (Table 2):

$$CsCu_9I_{10} \Leftrightarrow \gamma\text{-CuI} + CsCu_2I_3$$

However, no significant X-ray diffraction patterns for $CsCu_9I_{10}$ quenched from 618 K (Table 1, series II) or from 550 K (Table 1, series I and III) were observed. In the range of composition $0 < x_{CsI} < 0.333$ diffractograms exhibited a mixture of γ−CuI and $CsCu_2I_3$ patterns (Figure 2) for samples quenched from a level above the invariant temperature as well as for those quenched from a level below it. It is possible that this compound is stable only in a high-temperature region and decomposes on cooling, but between 604.8 K and about 320 K a respective invariance has not been found.

Thermal effects associated with the polymorphic transitions of CuI (β-CuI ⇔ liquid + α-CuI and γ-CuI ⇔ liquid + β-CuI) are observed only up to around 1 mol % CsI and 10 mol % CsI, respectively (Figure 1).

The invariant temperature 677.9 K is practically the same as the $\alpha \Leftrightarrow \beta$ transition temperature in CuI at 679.1 K given in ref 10. This may indicate that limiting solid solutions of CsI in α-CuI are negligible (Table 2). On the contrary, the invariant temperature 651.3 K is higher than the temperature of the $\beta \Leftrightarrow \gamma$ transition in solid CuI, 642.8 K, which is given in ref 10. This may indicate some solubility of CsI in β-CuI and in γ-CuI, probably not exceeding 2 mol % and 5 mol %, respectively (Table 2).

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