

## THE PHASE DIAGRAMS OF MIXTURES OF CuI WITH ZnI<sub>2</sub>, CdI<sub>2</sub> AND HgI<sub>2</sub>

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### ABSTRACT

The systems CuI–ZnI<sub>2</sub>, CuI–CdI<sub>2</sub> and CuI–HgI<sub>2</sub> resemble each other very closely, all exhibiting three broad regions of solid solutions based on the  $\alpha$ -,  $\beta$ - and  $\gamma$ -CuI modifications. In the case of the CuI–ZnI<sub>2</sub> and CuI–HgI<sub>2</sub> systems, compounds with an ordered distribution of the Cu<sup>+</sup> and Me<sup>2+</sup> cations crystallize at low temperatures from the  $\gamma$  solid solution (space group  $F\bar{4}3m$ , with a disordered distribution of cations). Cu<sub>2</sub>ZnI<sub>4</sub> and Cu<sub>2</sub>HgI<sub>4</sub> crystallize in the space group  $I\bar{4}2m$  with the lattice parameters  $a = 605.7(1)$  pm,  $c = 1188.3(3)$  pm, and  $a = 609.0$ ,  $c = 1223.0$  pm, respectively (Hahn et al., *Z. anorg. allg. Chem.*, 279 (1955) 271).

### INTRODUCTION

In recent years, many electrochemical measurements have been performed on CuI–M<sup>n+</sup>I<sub>n</sub> mixtures during searches for new copper superionic conductors. However, detailed information on the respective phase diagrams is still lacking. It appears that thorough investigations of the CuI–M<sup>n+</sup>I<sub>n</sub> systems are necessary to obtain information about the existence of new ternary copper compounds and their homogeneity ranges. This paper is part of a study on this topic and presents the phase diagrams of mixtures of CuI with the iodides of the elements zinc, cadmium and mercury.

According to Miyake et al. [1], CuI transforms at 642 K from the cubic zinc-blende-structure ( $\gamma$ -CuI) into the hexagonal wurtzite-type ( $\beta$ -CuI).  $\beta$ -CuI changes at 680 K into  $\alpha$ -CuI which again has the cubic lattice of the zinc-blende-type. For application as a superionic conductor, the influence of the addition of MI<sub>2</sub> on the homogeneity range and the transition temperature of  $\alpha$ -CuI is important.

Alexander and Riley [2] proposed a composition–temperature diagram for the CuI–ZnI<sub>2</sub> system. They suggest that, at room temperature, compositions with more than 40 mol.% CuI are solid solutions which transform at 423 K into solid solutions with ionic conduction. At 573 K, a new structure or a decomposition of this solid solution occurs. Materials between 10 and

30 mol.% CuI consist of CuI and ZnI<sub>2</sub>. Their results with regard to the existence of Cu<sub>2</sub>ZnI<sub>4</sub> are not convincing, because they observed the X-ray reflections of ZnI<sub>2</sub> in the X-ray pattern of a sample with 66 mol.% CuI, heated to 473 K and then quenched. Obviously the sample has been quenched from a two-phase region. On the other hand, samples cooled slowly from the melt to ambient temperature were solid solutions, according to their X-ray reflection patterns.

In an early work, Herrmann (3) found that CuI and CdI<sub>2</sub> form a complete series of solid solutions with a minimum in the liquidus at 90 wt.% CdI<sub>2</sub> and 623 K. He reports one transformation in CuI. Its temperature is depressed by the addition of CdI<sub>2</sub> from 687 K for pure CuI to 533 K at 90 wt.% CdI<sub>2</sub>. A similar shape of the liquidus line and decrease in the transformation temperature was observed by Lal and Srivastava [4]. In contrast, Wagner [5] measured a maximum solubility of only 6 mol.% CdI<sub>2</sub> in CuI at 573 K. The measurements of the electrical conductivity by Lal and Srivastava [4] and by Matsui and Wagner [6,7] indicate that the phase transformation which occurs between 687 and 533 K in the CuI-CdI<sub>2</sub> system is accompanied by a change from electronic to ionic conductivity. Both groups observed a decrease in the  $\alpha$ - $\beta$  and  $\beta$ - $\gamma$  transformation temperatures with increasing CdI<sub>2</sub> content. The conclusion of Matsui and Wagner on the topology of the phase diagram is doubtful, because the electrical conductivity of mixtures is not only influenced by the phase diagram but also by impurities and by the methods of preparing the sample. No investigations were performed on the CuI-HgI<sub>2</sub> system. The system is known to contain the compound Cu<sub>2</sub>HgI<sub>4</sub> [8]. It transforms at 339.6 K [9] from an ordered tetragonal modification with space group *I42m* [10] into a disordered cubic structure.

## EXPERIMENTAL

ZnI<sub>2</sub> was prepared by sealing and melting stoichiometric amounts of the components (Zn: Preussag 99.999%; I<sub>2</sub>: Merck, sublimed twice) in an evacuated silica ampoule. CuI, CdI<sub>2</sub> and HgI<sub>2</sub> (Merck) were used after drying in a vacuum at 400 K. The samples were prepared by mixing the constituent iodides in concentration steps of 5 mol.%. The mixtures were sealed under vacuum in silica ampoules, then melted, homogenized by shaking, and annealed at appropriate temperatures for six weeks.

Our apparatus and method of differential thermal analysis have already been described [11]. The heating rate was 10 K min<sup>-1</sup>, the accuracy of the liquidus temperatures is  $\pm 5$  K and that of the three phase equilibria lines is  $\pm 2$  K. A differential scanning calorimeter (DSC) (990 thermal analyzer, DuPont) was used for the investigation of the low temperature reactions. X-ray data of the powdered samples were obtained with a Guinier camera

(620, Fa. Huber). High temperature X-ray data were measured with a Simon-Guinier camera, using Cu  $K\alpha_1$  radiation in both cases.

## RESULTS

The  $T-x$  diagrams CuI-IIbI (IIb = tn, Cd, Hg), presented in Figs. 1, 4 and 5, were constructed from the DTA, DSC, dilatometric and X-ray measurements.

The CuI-ZnI<sub>2</sub> system (Fig. 1) is governed by the high solid solubility of ZnI<sub>2</sub> in all CuI modifications at higher temperatures. The solubility of ZnI<sub>2</sub> in  $\gamma$ -CuI increases drastically from approximately 2 mol.% at ambient temperature to 37 mol.% ZnI<sub>2</sub> at 418 K. Depending on the composition, the  $\gamma$  solid solution transforms into a solution with  $\beta$ -CuI structure between 653 (95 mol.% CuI) and 575 K (66 mol.% CuI). The  $\beta$  phase is formed by an eutectoid reaction from ZnI<sub>2</sub> and the  $\gamma$  solid solution at 575 K. Its homogeneity range extends to 50 mol.% ZnI<sub>2</sub> at 665 K. At 778 K and 85 mol.%, the  $\beta$  phase decomposes peritectically into  $\alpha$ -CuI and melt. The solubility of ZnI<sub>2</sub> in  $\alpha$ -CuI has a maximum of 10 mol.% at 778 K. The solubility of CuI in ZnI<sub>2</sub> is approximately 3 mol.%.

Below 425 K, the  $\gamma$  solid solution undergoes an order-disorder transformation. It decomposes into  $\gamma$ -CuI with a low ZnI<sub>2</sub> content and Cu<sub>2</sub>ZnI<sub>4</sub>.

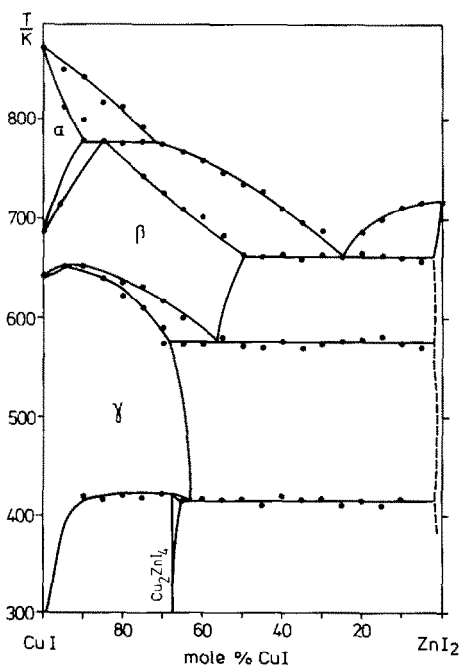


Fig. 1. The phase diagram for CuI-ZnI<sub>2</sub>.

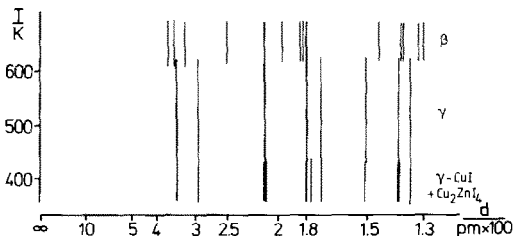


Fig. 2. High temperature X-ray photograph of a sample with 70 mol.% CuI.

This reaction is revealed by a high temperature X-ray photograph (Fig. 2). The X-ray pattern of  $\text{Cu}_2\text{ZnI}_4$  was indexed with tetragonal symmetry and the lattice parameters were  $a = 605.7(1)$  and  $c = 1188.3(3)$  pm (Table 1). This could be simulated by the program LAZY-PULVERIX [12], assuming that  $\text{Cu}_2\text{ZnI}_4$  crystallizes in the same space group as  $\text{Cu}_2\text{HgI}_4$  [10]. The very good agreement of experimental and simulated intensities and  $d$  values of the X-ray reflections verified the assumption that  $\text{Cu}_2\text{ZnI}_4$  (Fig. 3) crystallizes in the space group  $I\bar{4}2m$ . Like  $\text{Cu}_2\text{HgI}_4$ ,  $\text{Cu}_2\text{ZnI}_4$  transforms at medium temperatures into a modification with space group  $F\bar{4}3m$  and a statistical distribution of  $\text{Cu}^+$  and  $\text{Zn}^{2+}$  ions on the tetrahedral lattice sites. This disordered modification is part of the homogeneity range of the  $\gamma$ -CuI mixed crystal.

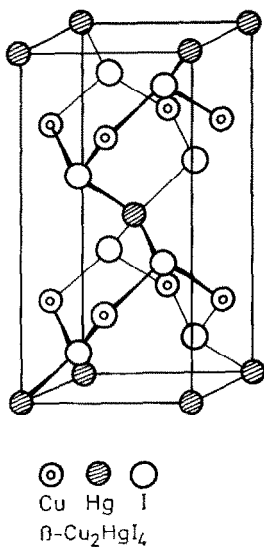


Fig. 3. Structure of  $\beta$ - $\text{Cu}_2\text{HgI}_4$  and  $\beta$ - $\text{Cu}_2\text{ZnI}_4$ .

TABLE 1  
X-ray data for  $\text{Cu}_2\text{ZnI}_4$

Number	$d_{\text{exp}}$ (pm)	$d_{\text{calc}}$ (pm)	$I/I_0$	(hkl)
1	539.8	539.6	20	(101)
2	428.5	428.3	10	(110)
3	347.7	347.4	100	(112)
4	331.3	331.5	10	(103)
5	302.8	302.8	40	(200)
6	297.2	297.1	20	(004)
7	269.2	269.8	10	(202)
8	264.3	264.1	20	(211)
9	244.0	244.1	10	(114)
10	224.4	223.6	10	(213)
11	214.0	214.1	100	(220)
12	212.0	212.0	60	(204)
13	198.6	199.0	10	(301)
14	191.6	191.5	10	(310)
		191.1		(302)
15	182.4	182.3	100	(312)
16	179.6	179.7	40	(116)
17	173.5	173.7	30	(224)
18	154.5	154.6	10	(323)
19	151.3	151.4	40	(400)
20	148.3	148.1	20	(207)
21	138.7	138.8	60	(332)
22	137.6	137.7	30	(316)
23	135.3	135.4	30	(420)
24	134.8	134.9	20	(404)
25	133.0	133.0	10	(227)
26	129.9	129.9	10	(307)
27	123.1	123.2	30	(424)
28	121.9	122.0	20	(228)
29	116.4	116.5	50	(512)
30	115.7	115.8	20	(336)
31	114.4	114.5	20	(1110)
32	107.0	107.1	30	(440)
33	106.0	106.0	10	(408)
34	102.3	102.3	60	(532)

$a = 605.7 \pm 0.1$  pm and  $c = 1188.3 \pm 0.3$  pm.

The phase diagram for  $\text{CuI}-\text{CdI}_2$  is presented in Fig. 4. It very closely resembles the previous one, except for the missing room temperature compound  $\text{Cu}_2\text{CdI}_4$ .  $\text{CdI}_2$  has a very limited solubility for  $\text{CuI}$ .  $\text{CuI}$  dissolves  $\text{CdI}_2$  in all modifications. The cubic  $\gamma$  phase has a maximum solubility of 25 mol.%  $\text{CdI}_2$  at 554 K. It transforms at 655 K into the hexagonal  $\beta$  solid solution, which forms eutectoidally at 554 K from  $\gamma$ - $\text{CuI}$  solid solution and

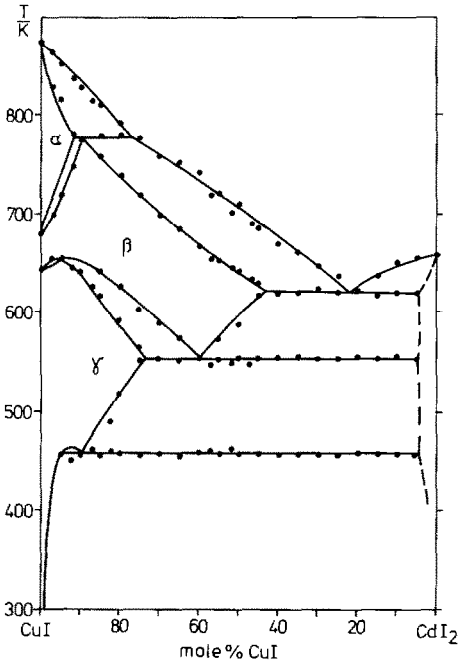


Fig. 4. The phase diagram for CuI–CdI<sub>2</sub>.

CdI<sub>2</sub>. The  $\beta$  solid solution decomposes peritectically at 780 K into  $\alpha$ -CuI and melt. Surprisingly CdI<sub>2</sub>-rich  $\gamma$ -CuI solid solutions decompose by a monotectoid reaction into  $\gamma$ -CuI and CdI<sub>2</sub> at 457 K. This is different from the behaviour of similar solid solutions in the system CuI–ZnI<sub>2</sub> (–HgI<sub>2</sub>), where a stoichiometric compound Cu<sub>2</sub>Zn(Hg)I<sub>4</sub> is formed at lower temperatures. The reason is probably the different site preferences of the Hg<sup>2+</sup>, Zn<sup>2+</sup> and Cd<sup>2+</sup> ions. Hg<sup>2+</sup> and Zn<sup>2+</sup> prefer tetrahedral, Cd<sup>2+</sup> prefers octahedral coordination. The substitution of Cu<sup>+</sup> by Cd<sup>2+</sup> ions is therefore an endothermic process which is only possible at higher temperatures. The unfavourable endothermic enthalpy contribution to the Gibbs energy can be compensated by the higher entropy of solid solutions with disordered cation sites, favouring the formation of these solutions at higher temperatures.

The CuI–HgI<sub>2</sub> (Fig. 5) and the CuI–ZnI<sub>2</sub> systems are very similar. CuI–HgI<sub>2</sub> shows two broad regions of solid solubility, with  $\gamma$ -CuI structure (maximum solubility 60 mol.% HgI<sub>2</sub> at 459 K) and  $\beta$ -CuI structure (maximum solubility 75 mol.% HgI<sub>2</sub> at 521 K). The  $\gamma$  mixed crystals transform at 650 K into the  $\beta$  modification. The  $\beta$  phase forms eutectoidally at 459 K from  $\gamma$ -“CuI” and HgI<sub>2</sub>, and decomposes peritectically at 735 K into  $\alpha$ -“CuI” (maximum solubility 10 mol.% HgI<sub>2</sub>) and melt. The solubility of CuI in HgI<sub>2</sub> is less than 1 mol.%. Below 346 K, the HgI<sub>2</sub>-rich  $\gamma$  solid solutions decompose into  $\gamma$ -CuI and the compound Cu<sub>2</sub>HgI<sub>4</sub> [10].

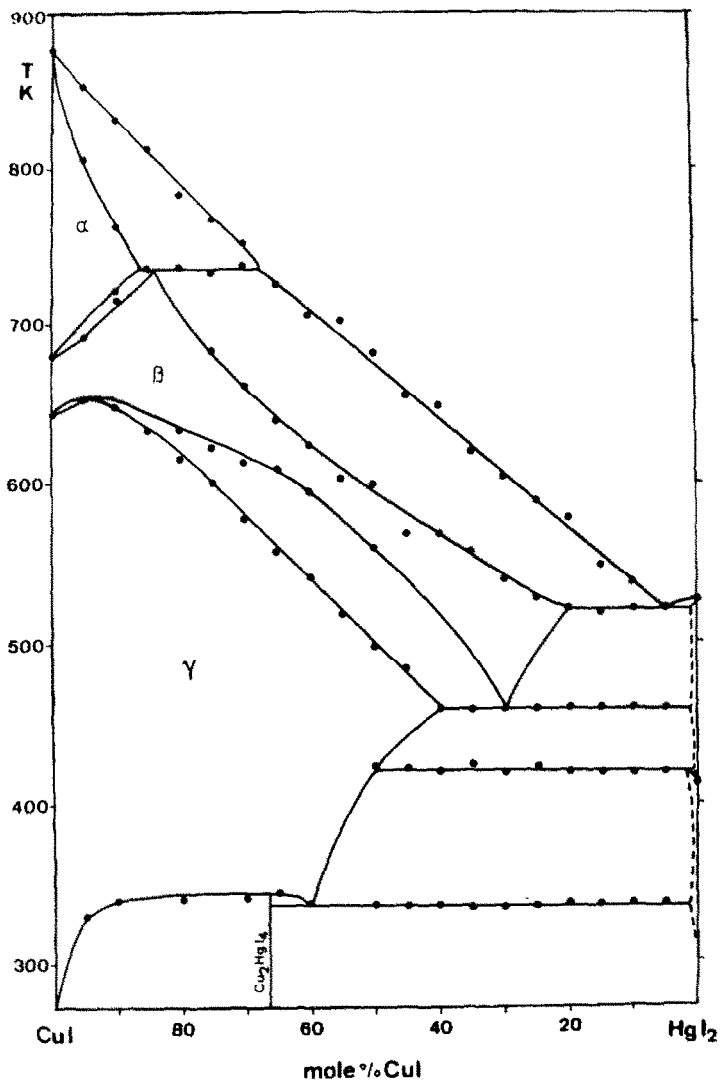


Fig. 5. The phase diagram for CuI-HgI<sub>2</sub>.

#### ACKNOWLEDGEMENT

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