Cerium – Copper – Zinc

Oksana Bodak†, Paola Riani

Introduction

In a series of consecutive investigations of the Ce-Cu-Zn ternary system [2004Pav1, 2004Pav2, 2005Pav] determined the isothermal section at 200°C. A number (not specified in the papers) of samples prepared by arc melting the elements (purity better than 99.9 mass%) was subsequently heat treated at 200°C for 600 h. Previous investigations of this system were directed to study thermal properties of $CeCu_xZn_{1-x}$ single crystals and their crystallochemical transition [2002Ish, 1989Uwa, 1988Fuj, 1988Uwa], crystalline electric fields (CEF) and magnetic structures in the $Ce(Cu_xZn_{1-x})_2$ system [1992Mor, 1992Gig1, 1992Gig2] and mechanical behavior of cerium-modified α-β brass at high temperatures was investigated by [1976Cha]. The crystal structure of CeCuZn equiatomic compound was refined by [2000For]. [2004Jia] investigated the Fermi-liquid behavior in $CeCu_{6-x}M_x$ (M = Ni, Zn) systems.
Experimental details of the phase diagram studies are summarized in Table 1.

Binary Systems

The assessed version of the Ce-Cu and Cu-Zn systems reported by [2002Per] and [2006Leb], respectively, are here accepted as edge boundary systems; the Ce-Zn binary system is accepted from [Mas2].

Solid Phases

Crystallographic data of all the unary, binary and ternary compounds are listed in Table 2. Notice that for the Ce_2Zn_{17} composition two structures have been reported in literature: Th_2Ni_{17} type [1967Ian] and Th_2Zn_{17} type [1987Sie]. It is not known, however, if both of them are stable and, eventually, their temperature and composition ranges of stability. In the Ce-Zn binary system reported by [Mas2] only the Th_2Zn_{17} type structure is cited. The crystal structure of the new ternary compound $Ce_2Cu_{5-5.7}Zn_{2-1.3}$ (τ_1) was determined by single crystal method [2005Pav]. It crystallizes in the $Ce_2Ni_5Zn_2$ structure type. [2000For] studied the crystal structures of a series of RECuZn equiatomic ternary compounds including CeCuZn. However, [2005Pav] tends to interpret CeCuZn as being the terminal composition of the $CeCu_{2-1}Zn_{0-1}$ solid solution. This interpretation is supported by the fact that the binary $CeCu_2$ and the ternary CeCuZn compounds have the same structure type.

Isothermal Sections

The isothermal section of the Ce-Cu-Zn ternary system at 200°C was investigated in the whole concentration range by [2005Pav]. Being the only experimental work available on phase equilibria in this system, it is reported in Fig. 1. However more experimental details should be given in order to evaluate its reliability. Presently, the following facts raise doubts concerning the results of [2004Pav1, 2004Pav2, 2005Pav]: the weight losses of Zn samples during arc-melting are not reported and annealing times of 600 h at 200°C seem to be rather short for samples close to the Ce-Cu axis. Also it is not clear how many samples were investigated to conclude the isothermal section.

Notes on Materials Properties and Applications

For the $Ce(Cu_xZn_{1-x})_2$ system the CEF (crystalline electric field) was measured by [1992Mor]. For the $CeZn_2$ two excitation transfers were identified at 15.7 and 37.5 meV (10 K). With increase of Cu content the energy transfers and intensities become weaker. For the $CeCu_2$ there is only one transfer at 150 K of 14 meV intensity. [2002Ish] stated that for $CeCu_xZn_{1-x}$ at x = 0.2 and 0.4 an antiferromagnetic ordering takes place, while at x = 0.6 - ferromagnetic order is observed (Fig. 2). Moreover, the ground level of 4f configuration of Ce also changed from quartet (x = 0.2) to doublet (x = 0.6).

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Table 1: Investigation of the Ce-Cu-Zn Phase Relations, Structures and Thermodynamics

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1976Cha]	Mechanical investigation, X-ray line broadening measurements	475°C ≤ T ≤ 675°C, $Ce_{0.07}Cu_{61.33}Zn_{38.6}$ (in mass%)
[1988Fuj]	Neutron diffraction	$CeCu_{1-x}Zn_x$ at $0 \le x \le 1$
[1989Uwa]	Neutron diffraction	–263°C ≤ T ≤ –123°C (from figure), $CeCu_{1-x}Zn_x$ at $0 \le x \le 1$
[1992Mor]	Neutron spectroscopy, magnetic measurements	–268°C ≤ T ≤ 27°C, $Ce(Cu_xZn_{1-x})_2$ at $0 \le x \le 1$
[2000For]	X-ray analysis	T = 750°C, CeCuZn
[2002Ish]	X-ray analysis, calorimetry	–271°C ≤ T ≤ 27°C, $CeCu_{1-x}Zn_x$, at x = 0.2, 0.4, 0.6
[2004Pav1]	X-ray analysis, WDS, EPMA	T = 200°C, $Ce(Cu_{1-x}Zn_x)_5$, at $0 \le x \le 1$
[2004Pav2]	X-ray analysis, WDS, EPMA	T = 200°C, $CeCu_{6-x}Zn_x$, at $0 \le x \le 0.84$
[2005Pav]	X-ray analysis, WDS, EPMA	T = 200°C, Ce-Cu-Zn, whole concentration range

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
$(Cu_{1-x}Zn_x)$	*cF*4 $Fm\bar{3}m$ Cu		$0 \le x \le 0.383$ at 454°C
		a = 369.612	at 35.84 at.% Zn and 300°C [V-C2]
(Cu) < 1084.62		a = 361.46	at 25°C [Mas2]
(δCe) 798 - 726	*cI*2 $Fm\bar{3}m$ W	a = 412	0 to 0.55 at.% Cu at 708°C [2002Per]
(γCe) 726 - 61	*cF*4 $Fm\bar{3}m$ Cu	a = 510.10	0 to 0.37 at.% Cu at 708°C [1994Sub]
(βCe) 61 - (–177)	*hP*4 $P6_3/mmc$ αLa	a = 308.10 c = 1185.7	at 24°C [2002Per]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(αCe) < –177	*cF*4 $Fm\bar{3}m$ Cu	*a* = 485	at –196°C [2002Per]
(Zn) < 419.6	*hP*2 $P6_3/mmc$ Mg	 *a* = 266.5 *c* = 494.70	dissolves up to 1.5 at.% Cu at 424°C [2006Leb] at 25°C [Mas2]
$Ce(Cu_{1-x}Zn_x)$	*oP*8 *Pnma* FeB	 *a* =737 *b* = 447 *c* = 642	$0 \le x \le 0.3$ at *x* = 0.3 from figure [2005Pav]
CeCu < 516		*a* = 719 *b* = 430 *c* = 623	at *x* = 0 [2002Per]
$Ce(Cu_{1-x}Zn_x)_2$	*oI*12 *Imma* $CeCu_2$	 *a* = 454.1 *b* = 722.9 *c* = 758.1	$0 \le x \le 0.5$ at *x* = 0.5 [2000For]
$CeCu_2$ < 817		*a* = 442.9 *b* = 706.1 *c* = 747.4	at *x* = 0 [2002Per]
$CeCu_4$ < 796	*oP*20 *Pnnm* $CeCu_4$	*a* = 458 *b* = 810 *c* = 935	at *x* = 0 [2002Per]
$Ce(Cu_{1-x}Zn_x)_5$	*hP*6 *P6/mmm* $CaCu_5$	 *a* = 522.6 *c* = 417.2	$0 \le x \le 0.63$ at *x* = 0.63 [2004Pav1]
$CeCu_5$ < 798		*a* = 514.8 *c* = 410.8	at *x* = 0 [Mas2, 1994Sub]
$\beta Ce(Cu_{1-x}Zn_x)_6$	*oP*28 *Pnma* $\beta CeCu_6$	 *a* = 810.88 *b* = 510.04 *c* = 1016.21	$0 \le x \le 0.14$ at *x* = 0, 22°C [1990Vrt]
		a = 815.4 *b* = 505.6 *c* = 1018.5	at *x* = 0.14 [2004Pav2]
$\beta CeCu_6$ 938 - (–43)		*a* = 810.09 *b* = 509.78 *c* = 1015.48	at *x* = 0, – 23°[1990Vrt]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
αCeCu$_6$ < –43	*oP*28 $P2_1/c$ αLaCu$_6$	*a* = 509.5 *b* = 1014.66 *c* = 809.31 β = 90.485°	at –73°C [1990Vrt]
		a = 508.92 *b* = 1013.26 *c* = 807.89 β = 91.148°	at –173°C [1990Vrt]
		a = 508.41 *b* = 1012.79 *c* = 807.31 β = 91.442°	at –263°C [1990Vrt]
β, CuZn 903 - 454	*cI*2 $Im\bar{3}m$ W	*a* = 295.39	36.1 to 55.8 at.% Zn, [Mas2, V-C2] at 47.5 at.% Zn
β′, CuZn < 468	*cP*2 $Pm\bar{3}m$ CsCl	*a* = 295.9′	44.8 to 50.0 at.% Zn, [Mas2] at 49.5 at.% Zn
γ, Cu$_5$Zn$_8$ < 835	*cI*52 $I\bar{4}3m$ Cu$_5$Zn$_8$	*a* = 886.9	57.0 to 70.0 at.% Zn, [Mas2, V-C2]
δ, CuZn$_3$ 665 - 548	*hP*3 $P\bar{6}$ CuZn$_3$	*a* = 427.5 *c* = 259.0	72.45 to 76.0 at.% Zn, [Mas2, V-C2]
ε, CuZn$_4$ < 574	*hP*2 $P6_3/mmc$ Mg	*a* = 274.2 *b* = 429.4	78.0 to 88.0 at.% Zn, [Mas2]
Ce(Cu$_x$Zn$_{1-x}$)	*cP*2 $Pm\bar{3}m$ CsCl	*a* = 390.5	$0 \le x \le 0.5$ at $x = 0.5$ from figure [2005Pav]
CeZn < 825		*a* = 369.7	at $x = 0$ [V-C2]
Ce(Cu$_x$Zn$_{1-x}$)$_2$	*oI*12 *Imma* CeCu$_2$	*a* = 462.0 *b* = 748.2 *c* = 752.0	at $x = 0.6$ [2005Pav]
CeZn$_2$ < 875		*a* = 463.9 *b* = 755.2 *c* = 751.0	at $x = 0$ [V-C2]
CeZn$_3$ < 820	*oP*16 *Pnma* YZn$_3$	*a* = 664.0 *b* = 462.0 *c* = 1044.0	[V-C2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
Ce_3Zn_{11} < 840	*oI*28 *Immm* La_3Al_{11}	*a* = 451.9 *b* = 1344.4 *c* = 888.3	[V-C2]
$Ce_{13}Zn_{58}$ < 870	*hP*142 *P*6_3*/mmc* $Gd_{13}Cd_{58}$	*a* = 1460.0 *c* = 1411.0	[V-C2]
$Ce(Cu_xZn_{1-x})_5$	*hP*6 *P6/mmm* $CaCu_5$	*a* = 540 *c* = 424	at *x* = 1 [2005Pav]
$CeZn_5$ < 885		*a* = 541.63 *c* = 426.47	at *x* = 0 [V-C2]
Ce_3Zn_{22} < 960	*tI*100 *I*4$_1$*/amd* Pu_3Zn_{22}	*a* = 894 *c* = 2133	[V-C2]
$CeZn_{11}$ < 795	*tI*48 *I*4$_1$*/amd* $BaCd_{11}$	*a* = 1066.2 *c* = 685.5	[V-C2]
Ce_2Zn_{17} < 980	*hP*38 *P*6_3*/mmc* Th_2Ni_{17}	*a* = 908.8 *c* = 885.6	see comments in section Solid Phase [V-C2]
	or		
	*hR*57 *R*$\bar{3}$*m* Th_2Zn_{17}	*a* = 909.07 *c* = 1328.47	[V-C2] single crystal data
* τ_1, $Ce_2(Cu_{5+x}Zn_{2-x})$	*hR*54 *R*$\bar{3}$*m* $Ce_2Ni_5Zn_2$	*a* = 499.8 to 507.8 *c* = 3692.4 to 3698.7	$0 \le x \le 0.7$ [2005Pav] Single crystal refinement

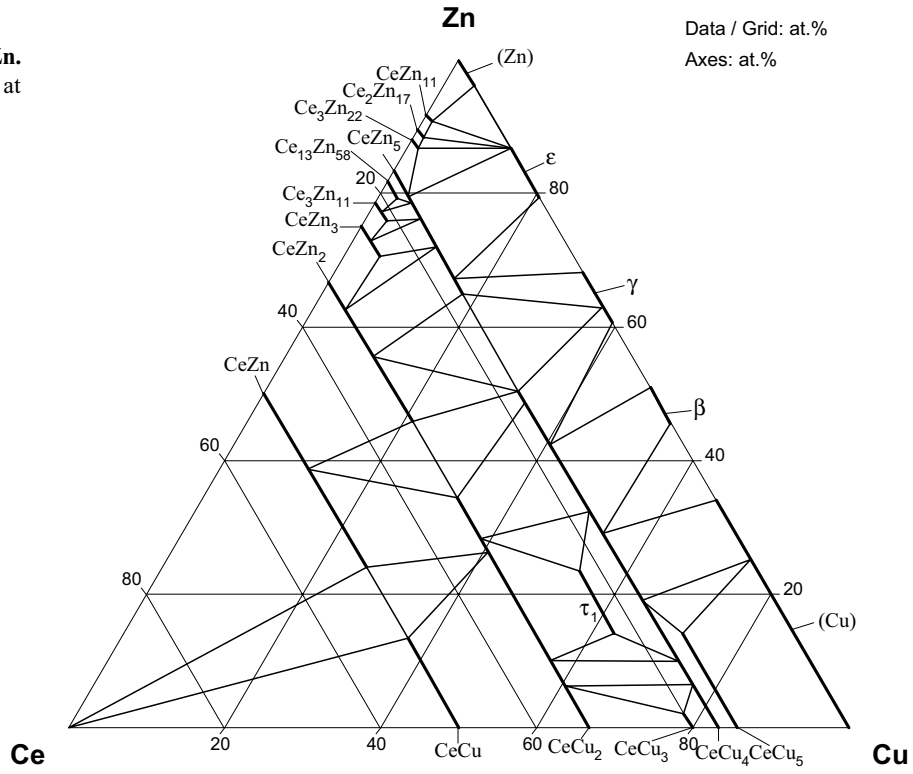

Fig. 1: Ce-Cu-Zn. Isothermal section at 200°C

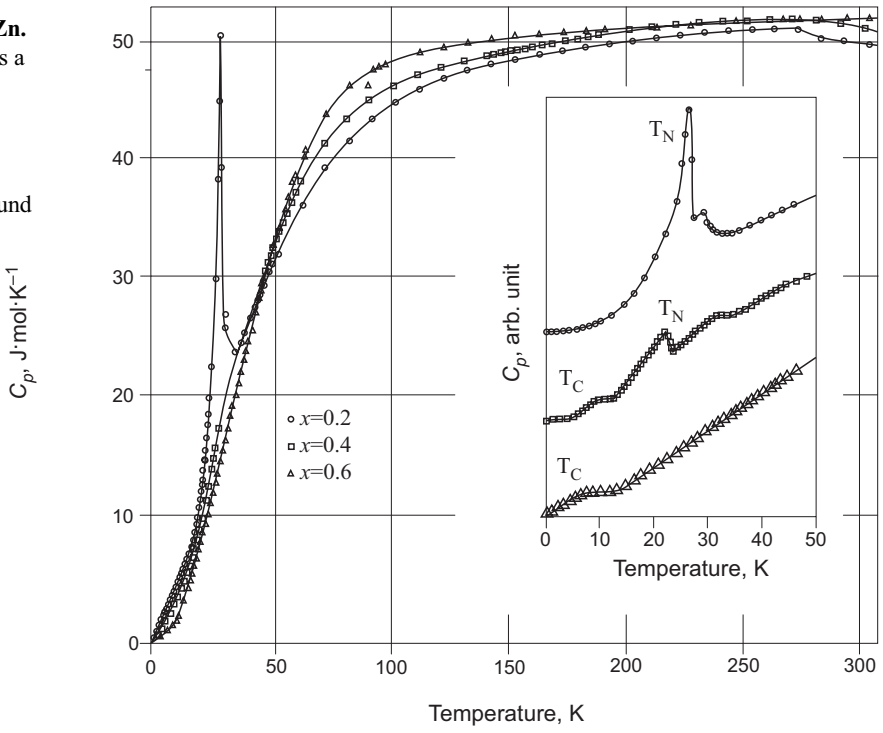

Fig. 2: Ce-Cu-Zn. Specific heat C_p as a function of temperature for $CeZn_{1-x}Cu_x$. The inset is a magnification around anomalies