Cerium – Copper – Nickel

Oksana Bodak†, Gabriele Cacciamani

Introduction

No complete phase diagram exists for the Ce-Cu-Ni ternary system. Phase relations in this system were studied by [1981Bod, 1986Kha] by investigating alloy samples prepared by arc melting from >99.99 mass% pure elements.
Most of the other investigations are concerned with the structural, magnetic and electronic properties of selected phases, especially $CeNi_xCu_{1-x}$ and $Ce(Ni_xCu_{1-x})_5$, often related to the variable valence of the Ce atoms.
Hydrogen storage properties and thermoelectric power of the $Ce(Ni_xCu_{1-x})_5$ phase have also been investigated.

Binary Systems

The Ce-Cu and Cu-Ni binary systems are accepted from the assessments by [2002Per] and [2002Leb], respectively. The Ce-Ni system is accepted from [Mas2].

Solid Phases

Crystallographic data of all the unary, binary and ternary phases are summarized in Table 1.
The crystal structure of two samples at the $CeNi_3Cu_3$ and $CeNi_4Cu_2$ compositions has been determined by [1998Moz1, 1998Moz2], by means of time-of-flight neutron diffraction. Whereas presented as two independent compounds by [1998Moz1, 1998Moz2], it is here tentatively assumed that the two samples belong to the same off-stoichiometric phase $Ce(Ni_{3+x}Cu_{3-x})$ having the $TbCu_7$ type structure. This should be a line compound where Cu and Ni atoms replace each other in the 2*e* dumb-bell site. This phase was not detected at 400°C by [1986Kha].
Lattice parameters of $Ce(Cu_{1-x}Ni_x)_5$ have been determined by [1982Pou, 1984Pop] as a function of the Cu/Ni ratio, by [1984Sin] at Cu/Ni equiatomic ratio, as a function of Ce content, and by [2001Sta] as a function of pressure.
Lattice parameter of the $Ce(Cu_{1-x}Ni_x)$ and $Ce(Cu_{1-x}Ni_x)_2$ solid solutions have been studied, as a function of composition, by [2000Esp] and [1977Olc], respectively.

Isothermal Sections

The Ce-Cu-Ni isothermal section at 600°C resulting from the combination of the data by [1977Olc, 1986Kha, 1997Sol, 1998Moz1, 1998Moz2] is sketched in Fig. 1. Main uncertainties, indicated by dashed lines, are related to the different extent of the solid solutions reported by different authors. Such differences seem larger than those which could be explained by the different temperature of the investigations considered.

Thermodynamics

The enthalpy of formation of the $Ce(Ni_xCu_{1-x})_5$ phase has been measured, as a function of composition, by drop calorimetry [1985Mey]. It follows a linear trend between –16 kJ·mol^{-1} at $x = 0.188$ and –33 kJ·mol^{-1} at $x = 1$. The same authors calculated the hydrogenation enthalpy of these alloys.
The enthalpy and entropy for hydrogen removal reach $H = 15.6$ (kJ·mol^{-1}) and $S = 72.3$ J·K^{-1}·mol^{-1} for the $CeNi_3Cu_2$ hydride, and $H = 17.3$ kJ·mol^{-1} and $S = 77.4$ J·K^{-1}·mol^{-1} for the $CeNi_{2.5}Cu_{2.5}$ hydride [1982Pou, 1984Ped]. According to [1984Sin] it is $H = 20.9$ kJ·mol^{-1} and $S = 81.7$ J·K^{-1}·mol^{-1} for the $Ce_{1.1}Ni_{2.5}Cu_{2.5}$ hydride. All data reported here are relative to a hydrogen capacity of 3 H atoms per formula unit.

Notes on Materials Properties and Applications

The $Ce(Ni_{1-x}Cu_x)$ phase has been investigated by several authors. [1997Sol] studied the low temperature magnetic and electric properties. Transition from Pauli paramagnetism to Kondo ferromagnetism and to antiferromagnetism as a function of Cu concentration was interpreted in terms of RKKY and Kondo interactions. Further studies performed by the same authors [2000Esp, 2000Sal, 2000Sol] leaded to the magnetic phase diagram reported in Fig. 2. Specific heat in the 0.2-300 K temperature range was measured by [2002Mar] and related to the magnetic properties.

Magnetic properties of $Ce(Ni_xCu_{1-x})_2$ have been measured by [1977Olc] for $0 < x < 1$. He found that Ni atoms are in a non-magnetic state and have filled d shells while Ce atoms are always in a trivalent state.

Hydrogen storage properties of $Ce(Ni_xCu_{1-x})_5$ have been studied by several authors. [1982Pou] found that, at intermediate Ni contents, absorption and desorption are very fast and can be performed at room temperature and hydrogen pressure lower than 10 atm. Moreover, hydrogenation enthalpy is lower than for $LaNi_5$. [1984Sin] found that at the $Ce_{1.1}(Ni_{0.5}Cu_{0.5})_5$ composition the H capacity is about 5.3 atoms per formula unit and the vapor pressure of the hydride is about 4 atm at room temperature.

[1984Ped] measured the magnetic susceptibility in $Ce(Ni_xCu_{1-x})_5$ alloys and their hydrides in the 4-300 K temperature range in an applied field of 20 kOe. They found that the phase exhibit Pauli paramagnetism at high Ni content, while, with Cu additions, the total susceptibility can be regarded as a combination of Pauli and Curie-Waiss paramagnetism associated with the Ce^{3+} ions. According to [1998Moz1] the trivalent character of the Ce atoms increases with Cu concentration.

Low temperature specific heat of $Ce(Ni_xCu_{1-x})_5$ ($0 < x < 0.8$) has been measured by [1985Ale] and results have been related to the mixed-valence state of Ce. Thermoelectric power of the same phase in the 4-900 K temperature range was investigated by [2001Kot] and related to the valence instability of Ce, with special attention to the transition from ordinary intermediate valence to saturated valence state.

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Table 1: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(Ni_xCu_{1-x})	*cF*4 *Fm*$\bar{3}$*m* Cu	 *a* = 356.655	$0 \le x \le 1$, dissolves up to 0.1 at.% Ce at 876°C [2002Per] at $x = 0.5$ [V-C2]
(Ni) < 1455		*a* = 352.40	at $x = 1$, 25°C [2002Per]
(Cu) < 1084.62		*a* = 361.46	at $x = 0$, 25°C [2002Per]
(δCe) 798 - 726	*cI*2 *Im*$\bar{3}$*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 [2002Per]
(Ce) 61 - (–177)	*hP*4 $P6_3/mmc$ La	*a* = 308.10 *c* = 1185.7	at 24°C [2002Per]
(αCe) < –177	*cF*4 *Fm*$\bar{3}$*m* Cu	*a* = 485	at –196°C [2002Per]
$Ce(Ni_xCu_{1-x})$	*oP*8 *Pnma* FeB	 *a* = 741.5 to 731.6 *b* = 456.4 to 448.6 *c* = 564.3 to 564.1	$0 < x < 0.8$ [1997Sol, 2000Sol] at $0 \le x \le 0.4$, $T < 10$ K. Neutron diffraction, Rietveld refinement [2000Esp]
CeCu < 516		*a* = 737.0 *b* = 462.3 *c* = 564.8	at $x = 0$ [2002Per]
$Ce(Ni_xCu_{1-x})_2$	*oI*12 *Imma* $CeCu_2$	 *a* = 443.3 to 434.9 *b* = 706.4 to 712.4 *c* = 747.2 to 735.1	$0 < x < 0.5$ at $0 \le x \le 0.5$ [1977Olc]
$CeCu_2$ < 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]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
$Ce(Ni_xCu_{1-x})_5$	*hP*6 *P*6/*mmm* $CaCu_5$		$0 \le x \le 1$ dissolves about 1 at.% Ce at $x = 0.5$ [1984Sin]
		a = 507.6 to 486.0 c = 407.6 to 399.6	at $0.2 \le x \le 1$ (non-linear variation) [1982Pou, 1984Ped]
		a = 514.6 to 487.4 c = 410.8 to 401.1	at $0 \le x \le 1$ (non-linear variation) [1984Pop]
		a = 508.6 to 488.2 c = 409.2 to 400.4	at $0.188 \le x \le 1$ (non-linear variation) [1985Mey]
		a = 493.2 to 460.5 c = 403.7 to 385.5	at $x = 0.6$, p = 0 to 40 GPa (from figure) [2001Sta]
$CeCu_5$ < 798		a = 514.8 c = 410.8	at $x = 0$ [2002Per]
$CeNi_5$ < 1345		a = 486 c = 399.6	at $x = 1$ [V-C2, Mas2, 1982Pou, 1984Ped]
$CeCu_6$ 938-(–43)	*mP*28 *Pnma* $\beta CeCu_6$	a = 810.88 b = 510.04 c = 1016.21	at 22°C [1990Vrt]
		a = 810.09 b = 509.78 c = 1015.48	at –23° [1990Vrt]
$\alpha CeCu_6$ < –43	*oP*28 $P2_1/c$ $\alpha LaCu_6$	a = 509.5 b = 1014.66 c = 809.31 β = 90.485°	at –73° [1990Vrt]
		a = 508.92 b = 1013.26 c = 807.89 β = 91.148°	at –173° [1990Vrt]
		a = 508.41 b = 1012.79 c = 807.31 β = 91.442°	at –263° [1990Vrt]
Ce_7Ni_3 < 505	*hP*20 $P6_3mc$ Fe_3Th_7	a = 992.6 c = 631.1	[Mas2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
$CeNi_{1-x}Cu_x$	*oC*8 *Cmcm* CrB	 *a* = 375.4 *b* = 1057.5 *c* = 437.6	$0 < x < 0.15$ at $x = 0$ [Mas2]
$CeNi_2$ < 830	*F*24 $Fd\bar{3}m$ Cu_2Mg	*a* = 722.46	[V-C2, Mas2]
$CeNi_3$ < 930	*hP*24 $P6_3/mmc$ $CeNi_3$	*a* = 498 *c* = 1654	[Mas2]
Ce_2Ni_7 < 1065	*hP*36 $P6_3/mmc$ Ce_2Ni_7	*a* = 490.5 *c* = 2438	[V-C2, Mas2]
* τ_1, $Ce(Ni_{1-x}Cu_x)_6$	*hP*8 *P*6/*mmm* $TbCu_7$	 *a* = 496.57 *c* = 406.69 *a* = 491.21 *c* = 405.68	$0.33 < x < 0.5$ at x =0.5 at $x = 0.33$ Neutron diffraction, Rietveld refinement [1998Moz1, 1998Moz2]

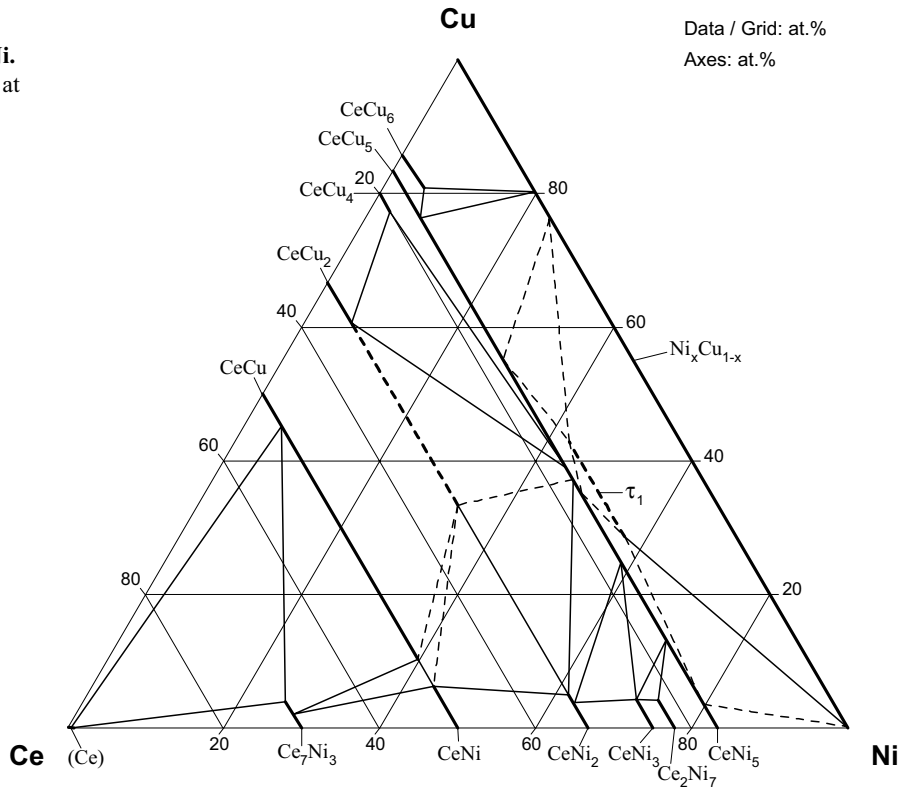

Fig. 1: Ce-Cu-Ni. Isothermal section at 600°C

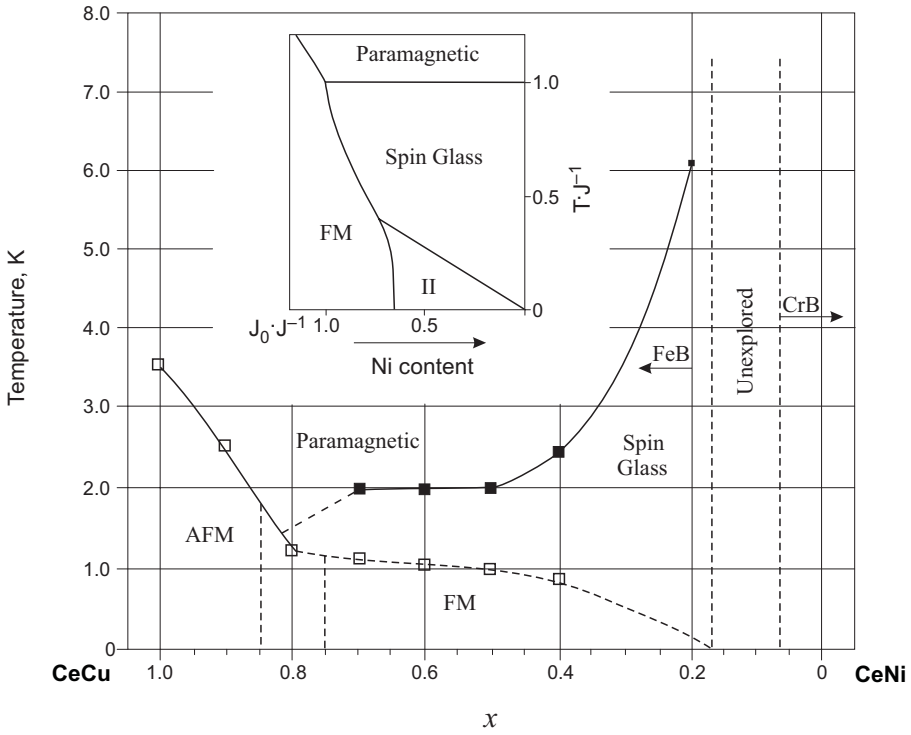

Fig. 2: Ce-Cu-Ni. Magnetic phase diagram for the $CeNi_{1-x}Cu_x$ vertical section as a function of the Cu concentration. Inset: Van Hemman classical phase diagram