Copper – Gadolinium – Tin

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Introduction

The phases of the system were studied mainly in the investigations aiming to find phases with unusual physical properties (mainly magnetic). As a result, almost all investigations were conducted not for the entire system, but rather for occurrence and properties of phases with particular stoichiometry, structural types, *etc.* in a series of analogous systems.
[1976Dwi] studied crystal structures of a series of compounds RE(Cu,Au)Sn (hereafter RE = rare earth metal), including GdCuSn. This phase was studied also by [1977Oes], [1983Kom] (magnetic properties), [1997Bar] and [1998For] (refinement of crystal structure and magnetic properties), [1997Bia] (Mössbauer study of magnetic properties of two Gd bearing phases). A series of the $RE_3Cu_4Sn_4$ phases including $Gd_3Cu_4Sn_4$ were studied by [1983Thi] and [1984Sko] (the latter authors wrote the formula as $RE_6Cu_8Sn_8$) for crystal structure and magnetic properties, as well as by [2000Sin] (magnetic ordering at low temperatures) and [2003Szy] (crystal structure and magnetic properties), [2004Szy] (magnetic properties). [1984Kom, 1990Sko] found 6 ternary phases numbered from 1 to 6. Neither noticeable homogeneity ranges nor solubility of a third component in the binary phases were detected. The crystal structures were determined only for two of them with formulas GdCuSn and $Gd_6Cu_8Sn_8$. A large series of phases with $CeNiSi_2$ type including $GdCuSn_2$ were investigated by [1990Fra] using X-ray powder diffraction and electron microprobe analysis. Investigation [1990Fra] showed deviation of the compound compositions from the stoichiometry and existence of the homogeneity ranges. Also the series of $RE_2Cu_4Sn_5$ phases was synthesized by [1992Kom]. In this work structure and magnetic properties, resistivity and thermo-emf were determined. Crystal structure and some physical properties of the ternary compound $GdCu_2Sn_2$ were studied by [1993Kac]. Crystal structure and magnetic properties of the ternary compound $GdCu_5Sn$ were investigated by [2001Mud].
Phase relations were studied in the only work [1984Kom] by the X-ray powder examination of 154 samples annealed at 400°C (670 K) (alloys composition and annealing time not specified). These data are briefly presented also in the reference book [1990Gla]. Most other works, even [1992Kom] with the participation of the same author, do not touch anyhow the phase relations.
[2000Sin] used low-temperature (2 to 40 K) heat capacity for $Gd_6Cu_8Sn_8$, in addition to resistivity and magnetization measurement, as a tool for studying magnetic ordering transitions in this phase.
The studies of the crystal structures of phases, phase relations and thermodynamic properties are referred in Table 1.

Binary Systems

For Cu-Gd edge the version [2006Rok], evaluated within the MSIT Binary Evaluation Program is accepted. Cu-Sn binary is accepted from [Mas2], and the Gd-Sn diagram was taken from a note [1995Oka], who modified somewhat the version of [1991Pal], essentially identical to [Mas2].

Solid Phases

Crystallographic information for the solid phases is summarized in Table 2. From binary phases only those appearing in the studied section of the ternary are included. Ternary compounds τ_1 to τ_6 correspond to those with numbers from 1 to 6 found in [1984Kom, 1990Sko]. Neither noticeable homogeneity ranges nor solubility of a third component in the binary phases were detected.
The solubility of Cu in the $GdSn_2$ phase was accepted after [1990Fra].
The structures of the τ_2, τ_3 and τ_6 phases remain unknown.

Isothermal Sections

Figure 1 presents isothermal section of the Cu-Gd-Sn system at 400°C. It is based on [1984Kom, 1990Sko], but with some corrections and additions by the present author. To bring the data [1984Kom, 1990Sko] in agreement with the accepted binaries, we had to replace the $GdCu_4$ phase by Gd_2Cu_9, add missed Gd_3Sn, Gd_8Sn_7 and Gd_3Sn_4 phases of the Gd-Sn edge and removed the "$GdSn_{2.75}$" phase. Finally, we restored missed solubility range of Sn in (Cu).
The τ_7 and τ_8 phases were also accepted and added. The tie-lines with participation of added phases were very tentatively estimated so as the equilibria established by [1984Kom, 1990Sko] were not destroyed (in all the cases it could be done uniquely). Also the distribution of the tie-lines on the fcc (Cu) phase is performed rather arbitrarily. All the added elements are given as uncertain by dashed lines.

Thermodynamics

No thermodynamic studies seem to be conducted except heat capacity measurements of $Gd_3Cu_4Sn_4$ at 2 to 40 K, performed by [2000Sin]. The results were used for determination of the temperatures of magnetic ordering. The entropy of magnetic transition was found to be ~3/4 of the theoretical value of $R\ln(7/2+1)$ per Gd atom.

Notes on Materials Properties and Applications

In the ternary compounds $Gd_3Cu_4Sn_4$, $GdCu_5Sn$ and GdCuSn anti-ferromagnetism was observed at low temperatures [1977Oes, 1993Kac, 1997Bar, 2001Mud, 2000Sin, 2002Sin, 2003Szy].

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Table 1: Investigations of the Cu-Gd-Sn Phase Relations, Structures and Thermodynamics

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1976Dwi]	Powder XRD	800°C, GdCuSn composition
[1983Kom]	Powder XRD	500°C, GdCuSn composition
[1983Thi]	XRD	$Gd_3Cu_4Sn_4$ composition
[1984Kom]	XRD (powder and single-crystal)	400°C (annealing time not given), 154 samples in the whole concentration range
[1984Sko]	XRD	$Gd_6Cu_8Sn_8$, annealed at 500°C, 700 h
[1990Fra]	XRD, EPMA	$GdCuSn_2$, annealed at 800°C (time not given)
[1992Kom]	XRD	400°C (annealed for 720 h), $Gd_2Cu_4Sn_5$
[1993Kac]	XRD	$GdCu_2Sn_2$
[1998For]	Powder XRD	$GdCu_5Sn$
[1998Pac]	Single-crystal XRD	GdCuSn
[2000Sin]	Low-temperature heat capacity	$Gd_3Cu_4Sn_4$, 2 to 40 K
[2001Mud]	Powder XRD	600°C (annealed for 1000 h), $GdCu_5Sn$

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(Cu) < 1084.62	*cF*4 $Fm\bar{3}m$ Cu	a = 361.46	at 25°C [Mas2]
(βGd) 1313 - 1235	*cI*2 $Im\bar{3}m$ W	a = 406	[Mas2]
(αGd) < 1235	*hP*2 $P6_3/mmc$ Mg	a = 363.36 c = 578.10	at 25°C [Mas2]
(βSn) 231.9681 - 13	*tI*4 *I*41/*amd* βSn	a = 583.18 c = 318.18	at 25°C [Mas2]
(αSn) < 13	*cF*8 $Fd\bar{3}m$ C (diamond)	a = 648.92	[Mas2]
$GdCu_6$ < 865	*oP*28 *Pnma* $CeCu_6$	a = 802.6 ± 0.5 b = 501.9 ± 0.2 c = 1006.2 ± 0.7	[2006Rok]
β$GdCu_5$ 925 - 870	*hP*6 *P6/mmm* $CaCu_5$	a = 503.6 c = 410.2 a = 501 c = 412	~16 to ~17.3 at.% Gd [2006Rok] at 39 K

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
αGdCu$_5$ < 870	*cF*24 $F\bar{4}3m$ AuBe$_5$	*a* = 706	~16 to ~17.3 at.% Gd [2006Rok]
Gd$_2$Cu$_9$ < 930	*h***	*a* = 500 *c* = 1390	[2006Rok]
Gd$_2$Cu$_7$ 870 - 825	-	-	[2006Rok]
Gd$_2$Cu < 860	*oI*12 *Imma* CeCu$_2$	*a* = 432.9 ± 0.4 *b* = 690.9 ± 0.5 *c* = 734.6 ± 0.8	[2006Rok]
GdCu < 870	*cP*2 $Pm\bar{3}m$ CsCl	*a* = 305.2	[2006Rok]
Gd$_3$Sn < 1173	-	-	[1995Oka]
Gd$_5$Sn$_3$ < 1243	*hP*16 $P6_3mcm$ Mn$_5$Si$_3$	*a* = 903.2 *c* = 659.5	[1995Oka], [1991Pal]
Gd$_5$Sn$_4$ < 1179	*oP*36 *Pmna* Sm$_5$Ge$_4$	*a* = 804.6 *b* = 1553 *c* = 819.2	[1995Oka], [1991Pal]
Gd$_8$Sn$_7$ < 1114	-	-	[1995Oka]
Gd$_{11}$Sn$_{10}$ < 1095	*tI*84 *I*4/*mmm* Ho$_{11}$Ge$_{10}$	*a* = 1167 *c* = 1715	[1995Oka], [1991Pal]
Gd$_3$Sn$_4$ < 995	-	-	[1995Oka]
GdSn$_2$ < 1140	*oC*12 *Cmcm* ZrSi$_2$	*a* = 442.8 *b* = 1641.0 *c* = 432.2 *a* = 442.4 *b* = 1670.0 *c* = 435.3	[1995Oka], [1991Pal] for GdCu$_{0.17}$Sn$_2$ composition [1990Fra]
Gd$_3$Sn$_7$ < 945	*oC*20 *Cmmm* Gd$_3$Sn$_7$	*a* = 445.97 *b* = 2651.63 *c* = 438.23	[1995Oka], [1991Pal]
βGdSn$_3$ 920 - 390	*cP*4 $Pm\bar{3}m$ AuCu$_3$	*a* = 467.6	[1995Oka], [1991Pal]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
αGdSn$_3$ < 390	*oC*16 *Amm*2 GdSn$_{2.75}$	*a* = 435.52 *b* = 440.39 *c* = 2204.4	identified by [1995Oka] with "GdSn$_{2.75}$" of [1991Pal] and [Mas2]
δ, ~Cu$_{41}$Sn$_{11}$ 590 - 350	*cF*416 $F\bar{4}3m$ Cu$_{41}$Sn$_{11}$	*a* = 1798.0	[Mas2]
ε, ~Cu$_3$Sn < 675	*oC*80 *Cmcm* Cu$_3$Sn	*a* = 552.9 *b* = 4775 *c* = 432.3	[Mas2]
η, ~Cu$_{44}$Sn$_{56}$ < 415	*hP*4 $P6_3/mmc$ NiAs	*a* = 419.0 *c* = 508.6	[Mas2]
* τ$_1$, GdCu$_5$Sn	*oP*28 *Pnma* CeCu$_5$Au	*a* = 825.0 *b* = 502.7 *c* = 1049.7	[1998For]
* τ$_2$, ~Gd$_3$Cu$_{13}$Sn$_4$	-	-	[1984Kom], [1990Gla]
* τ$_3$, ~GdCu$_7$Sn$_2$	-	-	[1984Kom], [1990Gla]
* τ$_4$, GdCuSn	*hP*6 $P6_3mc$ NdPtSb	*a* = 453.41 *c* = 736.3	[1998Pac]
* τ$_5$, Gd$_6$Cu$_8$Sn$_8$	*oI*22 *Immm* Gd$_6$Cu$_8$Ge$_8$	*a* = 1473.7 *b* = 694.6 *c* = 447.4	[1984Sko]
* τ$_6$, ~Gd$_3$Cu$_6$Sn$_{11}$	-	-	[1984Kom], [1990Gla]
* τ$_7$, GdCu$_2$Sn$_2$	*tP*20 *P*4/*mmm* CaBe$_2$Ge$_2$	*a* = 430.8 *c* = 1032.4	[1993Kac] sample with admixtures of several other phases
* τ$_8$, Gd$_2$Cu$_4$Sn$_5$	*tP*44 *I*4*mm* Sm$_2$Cu$_4$Sn$_5$	*a* = 439.2 *c* = 2489	[1992Kom]

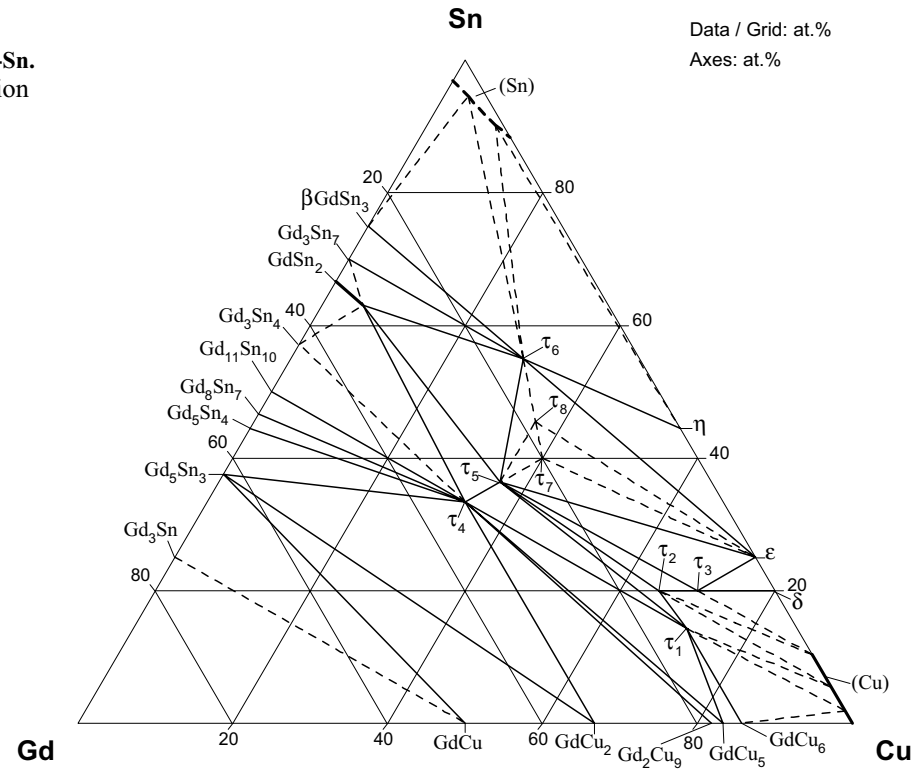

Fig. 1: Cu-Gd-Sn. Isothermal section at 400°C