Copper – Gallium – Manganese

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Introduction

There is a few literature data on the Cu-Ga-Mn phase diagram. [1961Gla, 1963Tes] revealed two ternary compounds in the Cu-Ca-Mn using X-ray investigations of crystal structure. These compounds were established to be the Laves phases with compositions (in at.%), 1) 33.33Mn-16.7Ga-50Cu ($MnCu_{1.5}Ga_{0.5}$), and 2) 33.3Mn-25Ga-41.7Cu ($MnCu_{1.25}Ga_{0.75}$). The first compound was of the $MgCu_2$ type and the second one was of the $MgZn_2$ type. [1986Mar] studied phase equilibria at 500°C in the region extended from the binary system Cu-Mn to the line connecting points of the binary alloys Cu-40 at.% Ga and Mn-62 at.% Ga. Using X-rays diffraction [1986Mar] confirmed existence of the two above mentioned compounds and discovered two new ternary compounds, $Mn_{1.05\text{-}1.42}Cu_{0.95\text{-}0.58}Ga$ with the crystal structure of the Ni_2In type and $Mn_{5.4}Cu_{0.6}Ga_5$ of the Ti_6Sn_5 type. Moreover, [1986Mar] found the compound $MnCu_{1.25}Ga_{0.75}$ to be characterized by a large homogeneity area so that its formula could be presented as $MnCu_{1.4\text{-}1.2}Ga_{0.6\text{-}0.8}$. Besides, [1986Mar] established a large solubility of Cu (up to 38 at.%) at 500°C in the binary Ga-Mn compound with the crystal structure of the Cr_5Al_8 type. According to the assumed binary Ga-Mn system [Mas2], this crystal structure belongs to the phase λ existing between 830 and 520°C only and, therefore, can not exist at 500°C of the isothermal section studied by [1986Mar].
[1988Bar, 1989Bar] studied two isothermal sections and three vertical sections in the Cu corner of the Cu-Ga-Mn phase diagram. The isothermal sections were at 700 and 550°C and the vertical sections were for constant contents of 65 mass% Cu, 75 mass% Cu and 6 mass% Mn. [1988Bar, 1989Bar] showed that ternary compounds $MnCu_{1.5}Ga_{0.5}$ and $MnCu_{1.4\text{-}1.2}Ga_{0.6\text{-}0.8}$ were in equilibrium with Cu-base solid solution at temperatures below 700°C.
Details of the experiments of the above mentioned works are described in Table 1.
[1986Gan] presented review on the work [1986Mar]. [1969Tes] presented review on the intermetallic compounds with structure of the Laves phases including two ternary compounds of the Cu-Ga-Mn system.

Binary Systems

The binary Cu-Ga, Cu-Mn and Ga-Mn systems are accepted from [2006Wat], [2005Tur] and [Mas2], respectively. Temperatures of the Mn polymorphous transformation are accepted after [2005Tur].

Solid Phases

Four ternary compounds were found in the studied part of the system. They are designated in the Table 2 as τ_1, τ_2, τ_3, τ_4. The compounds τ_1 and τ_4 are of constant composition. The compound τ_2 extends from ~20 to ~27 at.% Ga at 33.3 at.% Mn. The compound τ_3 extends from ~35 to ~47 at.% Mn at 33.3 at.% Ga. Crystal structures and lattice parameters of the ternary, binary and unary phases are shown in Table 2.

Invariant Equilibria

Three invariant four-phase equilibria were established in Cu rich alloys of the Cu-Ga-Mn system in the solid state [1989Bar]. Two of them are of the transition type and one of them is of the eutectoid type. They are $\beta + \tau_1 \rightleftharpoons (\gamma Mn_xCu_{1-x}) + \tau_2$ at 601 ± 5°C, $\beta + (\gamma Mn_xCu_{1-x}) \rightleftharpoons \zeta + \tau_2$ at 540 ± 5°C, $\beta \rightleftharpoons \gamma + \zeta + \tau_2$ at 520 ± 5°C. Compositions of the phases taking part in the equilibria were not determined.

Isothermal Sections

Isothermal section at 700°C converted into at.% is shown in Fig. 1 after [1988Bar]. It is reasonable to notice that the β phase is stable only at high temperatures and can not be retained after quenching to room temperature. During quenching the β phase undergoes “massive” transformation. Depending on the

composition β phase is transformed into (γMn_xCu_{1-x}) "massive" phase or into ζ "massive" phase. Samples of the alloys where "massive" transformation proceeded had structure with a specific plate-like morphology. Existence of this (γMn_xCu_{1-x}) massive phase confirmed by X-ray and microscopy methods can be considered as proof of the β phase existence at high temperatures.
Isothermal section at 550°C converted into at.% is shown in Fig. 2 [1988Bar] after corrections made for consistency with the Cu-Ga and Cu-Mn binary systems.
Isothermal section at 500°C is shown in Fig. 3 after [1986Mar] with some correction. Since the binary Ga-Mn system [Mas2] accepted in the present assessment differs from that accepted by [1986Mar] at the concentrations above 30 at.% Mn, the phase equilibria in the section at 500°C in the part adjoining to the Ga-Mn side are constructed speculatively and, therefore, shown at these concentrations by dashed lines. It is necessary to notice that the solid solution based on the λ compound with the structure of the Cr_5Al_8 type does not lie on the Ga-Mn side at 500°C.

Temperature – Composition Sections

Two vertical sections of the phase diagram for the Cu constant contents of 65 and 75 mass%, respectively, converted to at.% are shown in Figs. 4 and 5 after [1989Bar]. Temperatures of the binary alloys are corrected to meet the accepted binary phase diagrams. There are some insignificant discrepancies between the positions of the phase boundaries in the vertical sections (Figs. 4, 5) and in the isothermal section at 500°C (Fig. 3). They are caused by some differences in the conditions of the sample preparation. The phase equilibria near the Cu-Mn side are not investigated and are not shown in Figs. 4 and 5.

Notes on Materials Properties and Applications

[1979Bru] determined electrical resistivity of liquid Cu-Ga alloys with 2 at.% Mn by dc-method. Experimental results were analyzed basing on the Fridel virtual bound state model. Authors concluded that there are two well split impurity bands for the whole range between liquid Cu and Ga.
[1975Gar1, 1975Gar2, 1975Zol] measured magnetic properties of the liquid Cu-Ga alloys containing 2 to 5 at.% Mn. Basing on the results of the experiments estimation of polarization of spins near Mn atoms was made. The Mn magnetic properties depended only on the conduction electron density.
The structure and magnetic properties of the Cu-Ga-Mn alloys were studied by [1949Ham, 2001Shi, 2004Oik]. According to [1949Ham], the alloy $Mn_{1.00}Cu_{1.97}Ga_{1.05}$ demonstrated feeble magnetism after quenching, influence of annealing on magnetism being very slight. The alloy had two-phase structure.
[2001Shi] found that the alloy $Mn_{49.5}Cu_{16.5}Ga_{34}$ is a ferromagnetic with canted-spin arrangement for $208 \leq T \leq 335$ K. The alloy exhibits an incommensurate magnetic state below 280 K. [2004Oik] investigated martensitic transformation and magnetic properties of the Cu-Ga-Mn alloys in limits 21 to 25 at.% Ga, 10 to 20 at.% Mn. The alloy containing 21 at.% Ga and 12-15 at.% Mn demonstrated thermoplastic martensitic transformation in ferromagnetic state associated with shape-memory effect. The effect was observed after annealing at 750°C for 12 h followed by quenching into ice water. Heating provided structure of the alloy to be single β phase.

Miscellaneous

[1953Gal] proposed formula for calculation of the magnetic moments of ferromagnetic materials. Satisfactory agreement between calculated and experimental data were obtained, including for the alloy $MnCu_2Ga$.
[1983Pal] determined Curie temperatures of the "homologous row" of the Heusler alloys. The alloy $MnCu_2Ga$ was included in the homologous row, although the alloy was not single-phase one according to [1949Ham, 1986Mar].

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Table 1: Investigations of the Cu-Ga-Mn Phase Relations, Structures and Thermodynamics

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1961Gla]	X-ray powder method	Crystal structure and lattice parameter of $MnCu_{1.5}Ga_{0.5}$ and $MnCu_{1.25}Ga_{0.75}$
[1963Tes]	Melting in electric furnace in soldered vacuum ampoules. Heat treatment at 600°C for 120 h and quenching. X-ray diffraction and powder method	Four alloys with 33.3 at.% Mn and 12; 16.7; 25.0 and 33.3 at.% Ga. Crystal structure and lattice parameter
[1986Mar]	Arc melting in Ag atmosphere, homogenization at 750°C for 600 h for alloys with < 45 at.% Ga. X-ray diffraction and powder method	22 binary alloys and more than 120 ternary alloys in the range of compositions up to 40 at.% Ga and 60 at.% Mn. Annealing at 500°C for 800 h and quenching in cold water. Isothermal section at 550°C. Crystal structure and lattice parameters.
[1988Bar]	Arc melting in He atmosphere. Homogenization at 700°C for 200 h and quenching. Microscopic observation, EMA, X-ray diffraction and powder method, microhardness and electrical resistivity measurements.	Cu-corner up to 40 Ga and 40 Mn (mass%), 60 alloys. Annealing at 550°C for 200 h and quenching. Isothermal sections at 700 and 500°C. Crystal structure and lattice parameters for two ternary compounds.
[1989Bar]	Arc melting in He atmosphere. Homogenization at 550 to 700°C for 200 h and quenching. Microscopic observation, EMA, X-ray diffraction, DTA.	Cu-corner up to 40 Ga and 40 Mn (mass%), 60 alloys. Three vertical sections at Cu = 75 and 85 (mass%) and Mn = 6 and Ga from 0 to 30 (mass%), 50 alloys.

Table 2: Crystallographic Data of Solid Phases

Phase Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(γMn_xCu_{1-x})	*cF*4 $Fm\bar{3}m$ Cu		$0 < x < 1$ [2005Tur] maximum solubility 20.6 at.% Ga at 620°C [2006Wat] and $x = 0$; dissolves up to ~33 at.% Ga at 820°C and $x = 1$ [Mas2]
(γMn) 1138 - 1087		$a = 386.0$	pure γMn [Mas2]
(Cu) < 1084.62		$a = 361.46$	pure Cu at 25°C [Mas2]
(δMn) 1246 - 1138	*cI*2 $Im\bar{3}m$ W		dissolves up to 13 at.% Cu at 1097°C [2005Tur] and 42 at.% Ga at 715°C [Mas2]
		$a = 308.0$	pure δMn at >1138°C [Mas2, 2005Tur]
(βMn) 1087 - 727	*cP*20 $P4_132$ βMn		dissolves up to 2.03 at.% Cu at 706°C [2005Tur] and 19.5 at.% Ga < 620°C [Mas2]
		$a = 631.5$	pure βMn [Mas2]
(αMn) < 727	*cI*58 $I\bar{4}3m$ αMn	$a = 891.26$	dissolves up to 2 at.% Ga [Mas2] pure αMn at 25 °C [Mas2]
(Ga) < 29.7741	*oC*8 *Cmc*a αGa	$a = 451.86$ $b = 765.70$ $c = 452.58$	pure Ga [2006Wat]
(γ_2Mn), $Mn_{1-x}Ga_x$ 1087 - ~700	*tI*8 *I*4/*mmm* Al_3Ti	-	$0 < x < 0.27$, $0.34 < x < 0.38$ at ~810-700°C [Mas2]
(γ_3Mn), $Mn_{1-x}Ga_x$ $\lesssim$720 ~760 - 620	*tP*4 *P*4/*mmm* AuCuI	 $a = 388.4$ $c = 369.0$	 $0.37 < x < 0.45$ $0.16 < x < 0.24$ at 40 at.% Ga [1986Mar]
ε (Ga-Mn) < 820	*tP*4 *P*4/*mmm* AuCuI	$a = 398.8$ $c = 358.6$	27 to 30 at.% Ga [Mas2] at 33.3 at.% Ga [1986Mar]
λ (Ga-Mn) 830 - 520	*hR*78 *R*3*m* Cr_5Al_8	-	~45 to 60.5 at.% Ga [Mas2]
η (Ga-Mn) < 600	-	-	50 to 60 at.% Ga [Mas2]

Phase Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
χ (Ga-Mn) < 480	*tP*14 *P*4/*mbm* -	-	~70 at.% Ga [Mas2]
φ (Ga-Mn) < 500	-	-	~76 to 78 at.% Ga [Mas2]
ω (Ga-Mn) < 410	*oC*26 *Cmcm* Al_6Mn	-	~82 at.% Ga [Mas2]
β, ~$Cu_4Ga(h_2)$ 915-616	*cI*2 $Im\bar{3}m$ W	 *a* = 296.71	19.3 to 27.45 at.% Ga at 22.8 at.% Ga and 672°C [2006Wat]
ζ, ~$Cu_4Ga(h_1)$ 620 - 325	*hP*2 $P6_3/mmc$ Mg	 *a* = 259.74 *c* = 424.41	20.5 to 22.5 at.% Ga at 22.8 at.% Ga and 25°C [2006Wat]
ζ′, ~$Cu_4Ga(r)$ < ~322	-	 *a* = 259.46 *c* = 424.48	21 to 22.4 at.% Ga, stability range questionable, structure most likely of distorted $D0_{19}$ type at 22 at.% Ga [2006Wat]
γ, $Cu_9Ga_4(h)$ 836 - 490	*cP*52 $P\bar{4}3m$ Cu_9Al_4	 *a* = 874.7 *c* = 886.44	29.5 to 34.7 at.% Ga at 32.13 at.% Ga and 604°C [2006Wat]
γ_1, $Cu_9Ga_4(r)$ < 645	*cP*52 $P\bar{4}3m$ Cu_9Al_4	 *a* = 873.87 *a* = 872.95	29.8 to 37.4 at.% Ga, ordered form of γ at 32 at.% Ga at 36 at.% Ga [2006Wat]
γ_2, ~Cu_2Ga < 485	*cP** $P\bar{4}3m$ or *oI*12 $CeCu_2$	 *a* = 873.73 *a* = 433 *b* = 687 *c* = 733	33.9 to 37.7 at.% Ga at 34.06 at.% Ga annealing at 800°C [2006Wat]
γ_3, ~Cu_3Ga_2 < 468	*cP** $P\bar{4}3m$	 *a* = 869.49	38.1 to 42.6 at.% Ga at 38.4 at.% Ga [2006Wat]
θ, $CuGa_2$ < 254	*tP*3 *P*4/*mmm* $FeSi_2$	 *a* = 283.0 *c* = 583.9	~64.6 to 66.7 at.% Ga at 67 at.% Ga [2006Wat]
κ, (Cu-Mn) < 700	*c***	-	[2005Tur]
$MnCu_3$ < 450	*c***	-	critical point at ~24.5 at.% Mn [2005Tur]
$MnCu_5$ < 410	*c***	-	critical point at ~17 at.% Mn, ~9 to 31 at.% Mn at 512°C [2005Tur]

Phase Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
* τ_1, $MnCu_{1.5}Ga_{0.5}$	*cF*24 $Fd\bar{3}m$ $MgCu_2$	a = 691.1 a = 689.5 a = 691.2	[1963Tes, 1969Tes] [1986Mar] [1988Bar]
* τ_2, $MnCu_{2-x}Ga_x$	*hP*12 $P6_3/mmc$ $MgZn_2$	 a = 494.1 c = 800.5 a = 490.9 to 494.2 c = 793.1 to 794.8 a = 491.8 c = 795.2	$0.68 < x < 0.8$ for $MnCu_{1.25}Ga_{0.75}$ [1963Tes, 1968Tes] for $MnCu_{1.4}Ga_{0.6}$ to $MnCu_{1.2}Ga_{0.8}$ [1986Mar] for $MnCu_{1.25}Ga_{0.75}$ [1988Bar]
* τ_3, $Mn_{2-x}Cu_xGa$	*hP*6 $P6_3/mmc$ Ni_2In	 a = 420.2 c = 535.3	$0.58 < x < 0.95$ for $Mn_{1.38}Cu_{0.62}Ga$ [1986Mar]
* τ_4, $Mn_{5.4}Cu_{0.6}Ga_5$	*hP*22 $P6_3/mmm$ Ti_6Sn_5	a = 834.3 c = 518.5	[1986Mar]

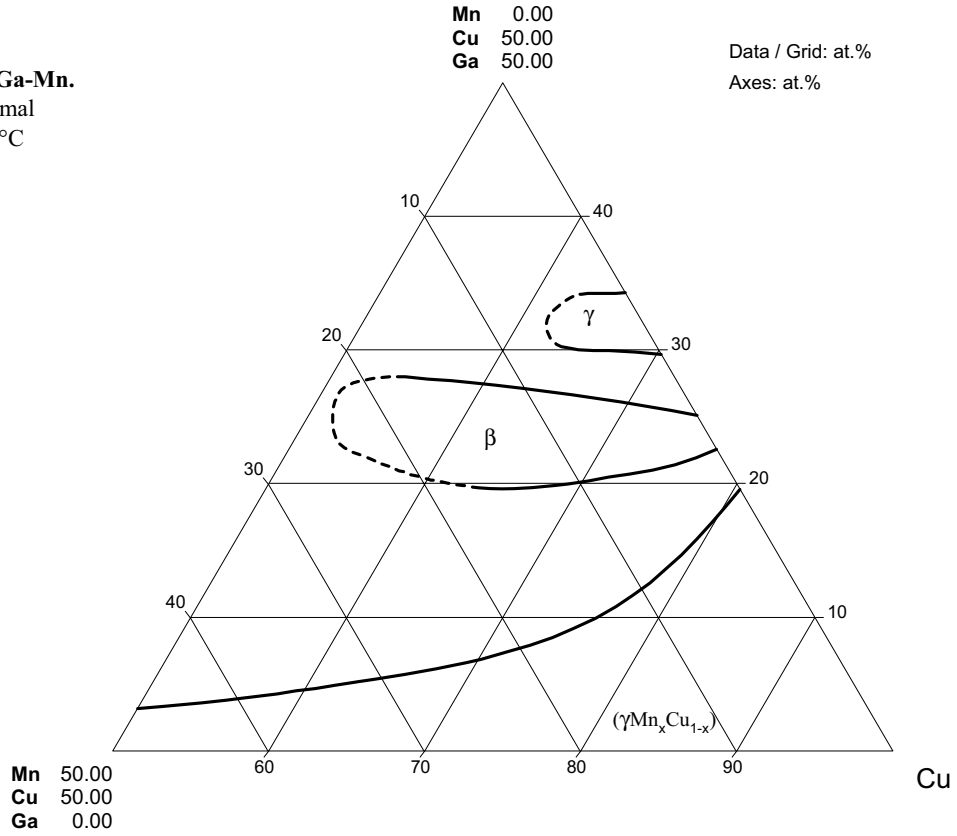

Fig. 1: Cu-Ga-Mn. Partial isothermal section at 700°C

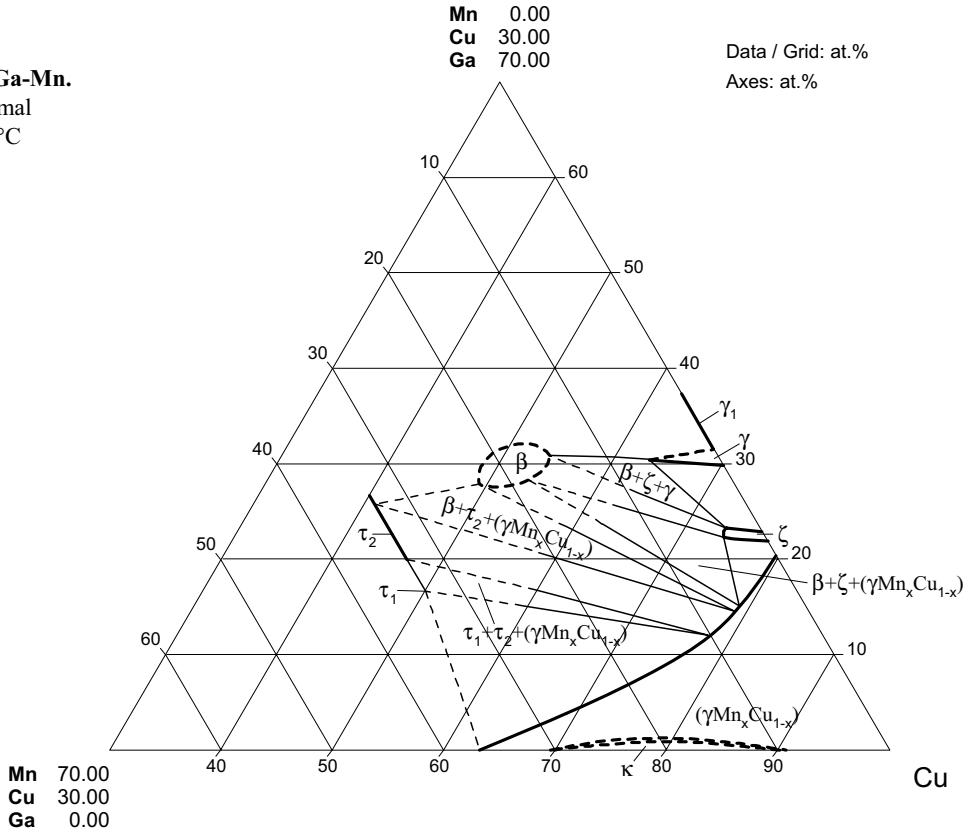

Fig. 2: Cu-Ga-Mn. Partial isothermal section at 550°C

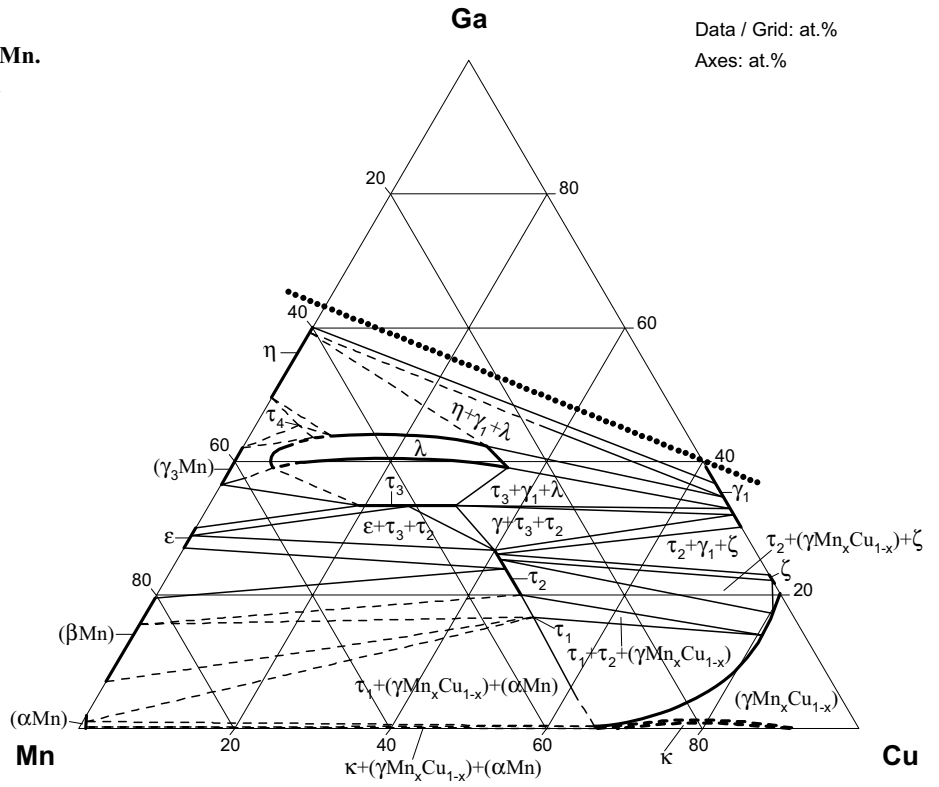

Fig. 3: Cu-Ga-Mn. Partial isothermal section at 500°C

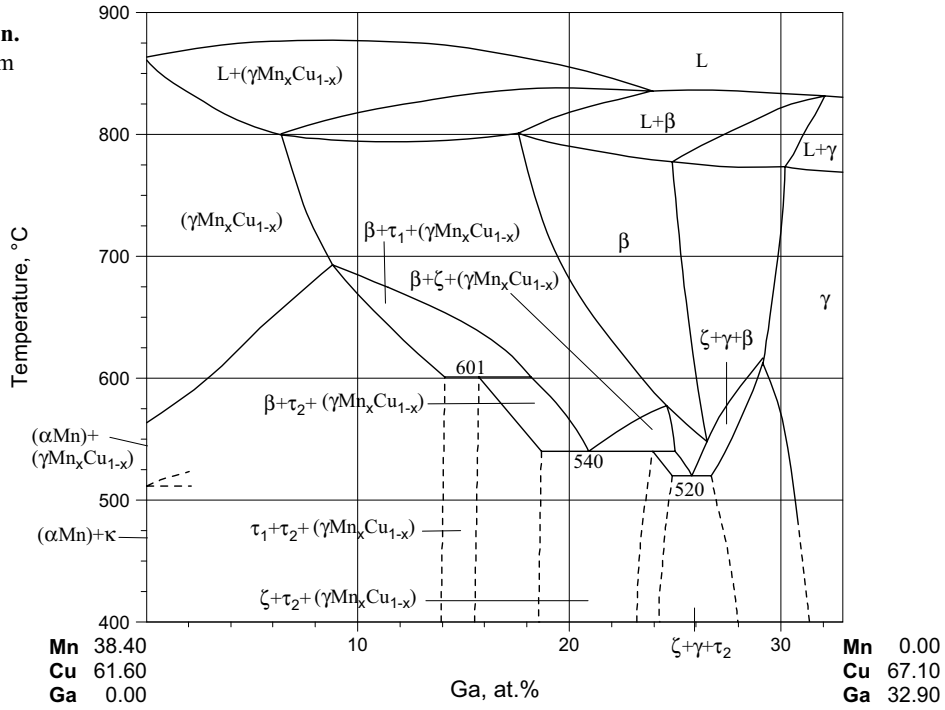

Fig. 4: Cu-Ga-Mn. Vertical section from Cu-38.4Mn to Cu-32.9Ga (at.%)

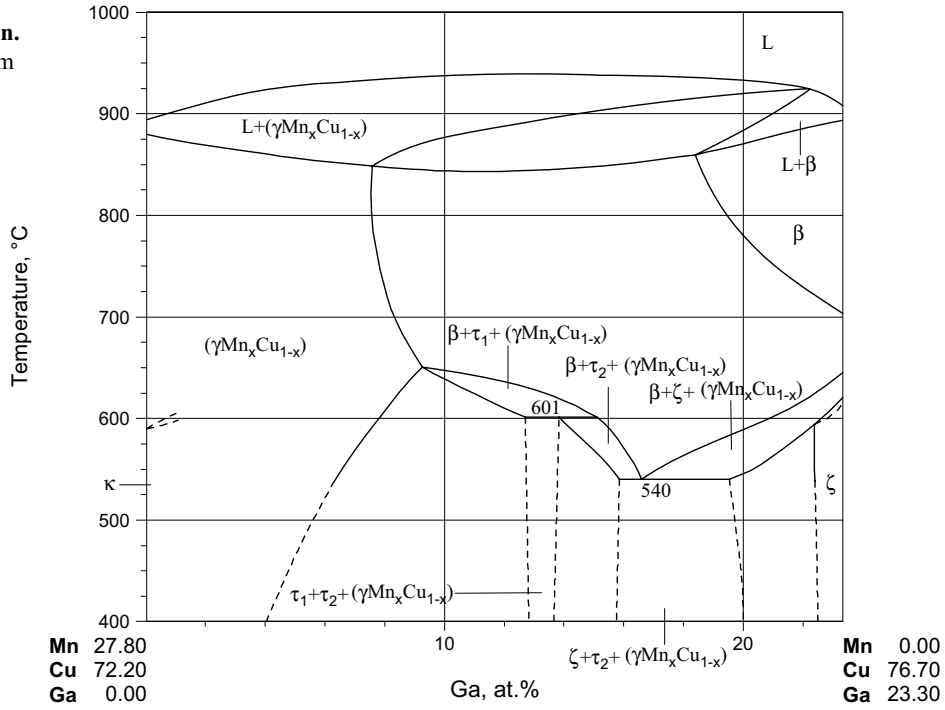

Fig. 5: Cu-Ga-Mn. Vertical section from Cu-27.8Mn to Cu-23.3Ga (at.%)