Copper – Germanium – Manganese

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Introduction

Compositions in the Cu-Ge-Mn system are important Cu-base alloys for electronics applications having a low electrical resistivity temperature coefficient.
Phase equilibria in the ternary Cu-Ge-Mn system have been investigated by [1961Coc, 1974Gav1, 1974Gav2, 1985Dri1, 1987Zav]. The crystal structures of the ternary compounds have been studied by [1961Gla, 1963Oxl, 1963Tes, 1965Aoy, 1986Zav, 1987Zav].
[1979Dri] reviewed the Cu-Ge-Mn system based on the work of [1963Tes, 1974Gav1, 1974Gav2].
The experimental work has been summarized in Table 1.

Binary Systems

The Cu-Mn, Ge-Mn and Cu-Ge binary phase diagrams are accepted from [2005Tur], [Mas2, 1990Gok] and [2002Fer], respectively. The temperatures of the Mn polymorphous transformations are accepted from [2005Tur].

Solid Phases

Seven ternary compounds have been discovered in the Cu-Ge-Mn system. The ternary Laves phase τ_1 (Mn_2Cu_3Ge or $MnCu_{1.5}Ge_{0.5}$) was initially found by [1961Gla] and later confirmed by [1963Tes, 1986Zav, 1987Zav]. According to [1986Zav], this compound has a wide homogeneity range due to both mutual substitution of Cu and Ge, and subtraction of Mn atoms. At 600°C the limits of the homogeneity region have been determined by [1987Zav] as 10 to 20 at.% Ge at 33 at.% Mn and 30 to 37 at.% Mn at 15 at.% Ge. According to [1986Zav], at this temperature, the composition 31 at.% Mn, 51.7 at.% Cu, 17.3 at.% Ge is located within the homogeneity range. [1974Gav1, 1974Gav2] report on the M-phase being in equilibrium with (Al) at 500 and 220°C, having the composition ~29 at.% Mn, 52 at.% Cu, 19 at.% Ge. Despite the crystal structure not being determined by [1974Gav1, 1974Gav2], the above composition allows it to be identified as τ_1.
[1963Oxl] reported the ferromagnetic Heusler phase $MnCu_2Ge$ (τ_2) with slight tetragonal deformation (c/a = 0.96). [1987Zav] confirmed the existence of the compound but failed to determine its crystal structure.
[1965Aoy] discovered a phase with the Ni_3Sn_2 type crystal structure existing close to the composition Mn_2CuGe_2 (τ_6). Some discrepancies exist in the results of [1965Aoy]. Thus, the phase is reported as ferromagnetic below 339 K. On the other hand, it is given as a high-temperature phase, stable at 600°C, and decomposing below this temperature into non-ferromagnetic phases. According to [1965Aoy], the composition Mn_2CuGe_2 is not an exact composition of the ternary compound, as traces of Ge and hexagonal phases were present in the sample of this composition. [1987Zav] determined the composition of the phase as $(Mn_{0.8}Cu_{0.2})_3Ge_2$, thus locating the composition Mn_2CuGe_2 in the three-phase region (Ge) + τ_6 + ε.
Ternary compounds τ_3, τ_4, τ_5 and τ_7 were found by [1987Zav] at 600°C. The crystal structure was not determined for the first two. Additional examination is required. The compound τ_7 extends into the ternary system along the line with constant Ge content of 28.5 at.% Ge, from ~2 to 30 at.% Mn.
At 400°C, τ_3, τ_6 and τ_7 were not observed by [1987Zav] suggesting their decomposition between 400 and 600°C. This should be studied in addition.
The T-phase, having the composition 30 at.% Mn, 5 at.% Cu, 65 at.% Ge, was observed by [1974Gav1, 1974Gav2] at 500 and 220°C in equilibrium with (γMn,Cu) and τ_1. It was confirmed to exist in equilibrium with ζ and τ_1 at 650°C by [1985Dri1]. The phase was not observed by [1987Zav] at 600°C, who assumed the T-phase to be the ternary compound $MnCu_2Ge$ (τ_2). This also needs examination.

The ternary phases τ_1 and τ_7 have a wide homogeneity region; other ternary compounds have a fixed composition.
The binary ζ phase (Cu_5Ge_3) has a large region of homogeneity which extends at 610°C from 0 to ~9 at.% Mn at 14 at.% Ge, and from ~12 to ~18 at.% Ge at 5 at.% Mn [1961Coc]. The binary ε_1 (Cu_3Ge) compound dissolves up to 10 at.% Mn at 600°C [1987Zav]. The binary η (Mn_5Ge_3) phase extends into the ternary system dissolving up to 15 at.% Cu [1987Zav]. All of the solid phases are presented in Table 2.

Invariant Equilibria

Three four-phase invariant equilibria were established in the Cu corner of the Cu-Ge-Mn system at 700, 675 and 655°C, respectively, by [1985Dri1]. They are all of eutectic type. In addition, there are two saddle eutectic points in the system, located at 695 and 720°C along the ζ - τ_1 and ζ - τ_2 sections, respectively. A partial reaction scheme for the Cu corner is shown in Fig. 1. The only liquid phase composition of all of the invariant reactions was determined by [1985Dri1]; for the reaction at 655°C as 18Mn-65.5Cu-16.5Ge (mass%), or 20.7Mn-55Cu-14.3Ge (at.%). The compositions of the solid phases in the equilibrium were determined as 10.3Mn-82.3Cu-7.4Ge (at.%) for (γMn,Cu); 2.8Mn-83.1Cu-14.1Ge (at.%) for ζ; 32.3Mn-52.2Cu-15.5Ge (at.%) for M or τ_1. In addition, the solubility of Mn in the ζ phase (about 3 at.%) seems to be too low, as does not correspond to that determined by [1961Coc, 1987Zav, 1974Gav1, 1974Gav2] at 610, 600 and 500°C, respectively, where it is about 9 at.%. Thus, at 655°C it also should be about 9 at.%.

Liquidus Surface

Only a Cu rich fragment of the liquidus surface was studied by [1985Dri1]. A tentative liquidus surface is shown in Fig. 2. The positions of the monovariant curves L + (Cu) $\rightleftharpoons$ ζ, L $\rightleftharpoons$ ζ + ε and of the eutectic point E_3 were located using experimental data [1985Dri1]. Other lines and critical points were drawn, supposedly taking into account the vertical sections [1985Dri1].

Isothermal Sections

Cu rich fragments of isothermal sections for 220, 500, 850°C and at 610°C were constructed by [1974Gav1, 1974Gav2] and by [1961Coc], respectively. Only [1987Zav] reported the isothermal section at 600°C for the whole concentration range. It is given in Fig. 3 with some corrections to maintain consistency with the accepted binary phase diagrams [Mas2, 1990Gok]. Therefore, in Fig. 3 the Mn_7Ge_3 κ-phase, is presented instead of the Mn_5Ge_2 phase. The Mn_5Ge_2 phase is absent at 600°C according to the accepted Ge-Mn binary. The section in Fig. 3 omits details of the Mn corner of the phase diagram because they were shown speculatively in the original article.

Temperature – Composition Sections

The vertical sections at 75 and 85 mass% Cu and at 2 mass% Mn were published by [1985Dri1]. The section at 2 mass% Mn considers the low solubility of Cu in the ζ phase, as discussed above, and is not accepted. Figures 4 and 5 show the vertical sections of the phase diagram for constant Cu contents of 75 and 85 mass%, respectively, given in at.%. These sections are made between points on the binary systems at Cu-22.58 at.% Ge and Cu-27.82 at.% Mn (Fig. 4) and Cu-13.38 at.% Ge and Cu-16.95 at.% Mn (Fig. 5). Minor corrections have been made to maintain consistency with the accepted binaries and the published isothermal sections. There is some disagreement between the vertical (Fig. 4) and isothermal (Fig. 3) sections in relation to the extension of phase boundaries at 600°C. The disagreement can be attributed to the possible deviation from equilibrium of the presented vertical section at temperatures below that of the invariant reaction. This part of the section shown in Fig. 4 was constructed taking into account only results of thermal analysis, studies of transformations involving the liquid phase and observations of the alloy structures obtained after thermal analysis experiments.

Notes on Materials Properties and Applications

Details of experimental studies are summarized in Table 3.
[1963Oxl, 1965Aoy] measured the magnetic properties of the $MnCu_2Ge$ alloy quenched from 800°C [1063Oxl] and the Mn_2CuGe_2 alloy cooled from 600°C [1965Aoy]. The Curie temperature was determined to be 300 K for $MnCu_2Ge$ and 339 K for Mn_2CuGe_2. [1965Aoy] established the temperature dependence of the inverse susceptibility of Mn_2CuGe_2.
The electrical properties and structure of Cu-Ge-Mn alloys (bulk samples) and films deposited via evaporation under vacuum for the use in microelectronics were investigated by [1975Boc, 1984Boc, 1985Dri2, 1990Boc]. A pronounced concentration gradient was observed across the thickness of the film as a consequence of the considerable difference between the saturation vapor pressures of copper and the alloying elements (Ge and Mn) during evaporation. The concentration gradient brought about a difference in the electric properties of the films and bulk samples. The films produced in this way consisted of three layers, each of them having a special function. The upper and lower layers were enriched in alloying elements whereas the middle layer was almost pure Cu. Therefore, the films showed high electrical conductivity, excellent adhesion with the substrate and good corrosion resistance.

Miscellaneous

Using X-ray phase analysis, [1977Pop] studied the structure of Cu-Ge-Mn alloys with 2 to 36 mass% Mn and 0.5 to 7 mass% Ge and the films deposited by the evaporation of these alloys in vacuum. The difference in phase compositions of the films and bulk samples were due to the presence of manganese oxides in the films. Another difference was a reduced effect of the alloying elements (Mn and Ge) on the lattice parameter of Cu in the films as compared with bulk samples.
[1978Nes] examined the effect of 0.5 to 4 mass% Mn additions on the saturated vapor pressure and evaporation rate of a Cu-Ge alloy with 9 mass% Ge, in the temperature range 830 to 1090°C. The experimental data indicated that the addition of more than 0.5 mass% Mn to the Cu-Ge alloy increased the total vapor pressure and evaporation rate of the alloy components in all cases.
Using neutron and X-ray diffraction, [1981Vin] investigated the influence of Ge (up to 8 at.%) on the structural layering of Cu-Mn alloys with 65 and 70 at.% Mn, and the low-temperature metastable f.c.c. → f.c.t. transformation. The dispersion factor had a decisive influence on this transformation.

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

Reference	Method/Experimental Technique	Temperature/Composition/ Phase Range Studied
[1961Coc]	Induction melting at 1300°C in graphite crucibles under Ar; casting in a mild steel mold; homogenization at 690°C for 10 to 14 d; annealing at 650 and 610°C, water quenched. Metallography, X-ray powder diffraction.	Cu corner, Ge and Mn up to 20 at.%. Isothermal section at 610°C, lattice parameters of ζ phase versus Ge concentration at 2.5, 5.0 and 7.5 at.% Mn, lines of constant axial ratio in ζ phase
[1961Gla] [1963Tes]	X-ray powder diffraction	$MnCu_{1.5}Ge_{0.5}$, crystal structure.
[1963Oxl]	Melting under argon at a few millimeters pressure, homogenization at 800°C, quenching down to room temperature, annealing at 200°C for 10 d. X-ray powder diffraction, magnetization.	$MnCu_2Ge$, crystal structure.
[1965Aoy]	Induction melting in Ar atmosphere; crushing, remelting in Tamman tubes; annealing at 600°C for 3 h under Ar, rapid or slow cooling. X-ray powder diffraction, magnetic susceptibility.	Alloy 40 at.% Mn, 20 at.% Cu, 40 at.% Ge (Mn_2CuGe_2), crystal structure, magnetic behavior.
[1974Gav1] [1974Gav2]	Induction melting; homogenization at 800°C for 24 h; rolling to 50 % deformation; annealing at 750°C for 2 h; annealing at 850, 500 and 220°C for 4, 48 and 500 h, respectively, water quenching. Metallography, X-ray diffraction, EMA, microhardness.	Cu corner, Ge up to 18 at.%, Mn up to 32 at.%. Isothermal sections at 850, 500 and 220°C
[1985Dri1]	Arc-melting under purified He atmosphere, homogenization at 650°C for 100 h, water quenching. Metallography, DTA, microprobe, microhardness.	Cu corner, Ge and Mn up to 30 mass%. Vertical sections at 75 and 85 mass% Cu, and at 2 mass% Mn, partial liquidus projection.
[1985Dri2]	Preparation as in [1985Dri1]. DTA, metallography, electrical resistivity.	Partial vertical section at 2 mass% Mn, Ge up to 15 mass%. Electrical resistivity of bulk and film specimens along the section.
[1986Zav]	Arc-melting in Ar atmosphere, homogenization at 600°C for 300 h. X-ray diffraction, crystal structure refinement.	Mn_2Cu_3Ge, crystal structure.
[1987Zav]	Arc-melting in an Ar atmosphere; homogenization at 600°C for 250 h and at 400°C. X-ray powder diffraction.	Isothermal section at 600°C, whole concentration interval (200 alloys).

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(γMn,Cu)	*cF*4 $Fm\bar{3}m$ Cu		
(Cu) < 1084.62		a = 361.46	pure Cu at 25°C [Mas2]
(γMn) 1138 - 1087		a = 386.0	pure γMn at 25°C [Mas2]
(δMn) 1246 - 1138	*cI*2 $Im\bar{3}m$ W	a = 308.0	pure δMn at >1138°C [Mas2, 2005Tur]
(βMn) 1087 - 707	*cP*20 $P4_132$ βMn	a = 631.5	pure βMn [Mas2]
(αMn) < 707	*cI*58 $I\bar{4}3m$ αMn	a = 891.26	pure αMn at 25°C [Mas2]
(Ge) < 938.3	*cF*8 $Fd\bar{3}m$ C(diamond)	a = 565.74	pure Ge [Mas2, 1990Gok, 2002Fer]
γ_3 ≤ 700	*c***	-	[2005Tur]
γ_2, $MnCu_3$ ≤ 450	*c***	-	[2005Tur]
γ_1, $MnCu_5$ ≤ 410	*c***	-	[2005Tur]
ε′, $Mn_{3.4}Ge$ 930 - 680	*hP*8 $P6_3/mmc$ Ni_3Sn	 a =536 ± 3 c = 432 ± 4 a = 538 ± 7 c = 431 ± 8	~22 to 23.5 at.% Ge, at 22.7 at.% Ge, at 23.5 at.% Ge [1990Gok]
ε′$_1$, $Mn_{3.4}Ge$ < 680	*tI*8 *I*4/*mmm* Al_3Ti	 a = 381 ± 6 c = 363 ± 1	~22 to 23.5 at.% Ge, at 22.7 at.% Ge [1990Gok]
ζ′, Mn_5Ge_2 953 - 620	*hP*128 $P\bar{3}c1$	 a = 718.5 c = 3917	~28.0 to ~30 at.% Ge, at 28.6 at.% Ge [1990Gok]
κ, Mn_7Ge_3 < 690	*o***	a = 612.8 b = 873.8 c = 2229.2	~30 at.% Ge [1990Gok]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
χ, Mn_2Ge 965 - 790	*hP*6 $P6_3/mmc$ Ni_2In	 a = 417.1 ± 0.1 c = 527.8 ± 0.2	32 to 34.4 at.% Ge, at 33.4 at.% Ge [1990Gok]
η, Mn_5Ge_3 < 966	*hP*16 $P6_3/mcm$ Mn_5Si_3	a = 719.7 c = 504.2	~37.5 at.% Ge [1990Gok]
Mn_3Ge_2, ≲ 796	*o***	a = 1320.1 ± 0.1 b = 1587.8 ± 0.4 c = 508.7 ± 0.1	at 40 at.% Ge [1990Gok]
ζ, ~Cu_5Ge_3 < 824	*hP*2 $P6_3/mmc$ Mg	 a = 259.93 c = 422.47	12.8 to 18.3 at.% Ge [2002Fer] at 17.2 at.% Ge [2002Fer]
ε, ~ Cu_3Ge 747 - 549.5	*hP*8 $P6_3/mmc$ $AsNa_3$	 a = 416.9 c = 749.9	23.1 to 23.5 at.% Ge, at 24 at.% Ge, 700°C [2002Fer]
$ε_1$, ~Cu_3Ge < 636	*hP*8 *Pmmn* βCu_3Ti	 a = 528 b = 422 c = 454	23.1 to 25.1 at.% Ge [2002Fer]
$ε_2$, Cu_3Ge 698 - 614	*cF*16 $Fm\bar{3}m$ BiF_3	a = 590.6	at 28.6 at.% Ge [2002Fer]
$τ_1$, Mn_2Cu_3Ge	*hP*12 $P6_3/mmc$ Mg_2Cu_3Si	a = 492.9 ± 0.1 c = 786.4 ± 0.2 a = 491.6 ± 0.1 c = 785.2 ± 0.2	for $MnCu_{15}Ge_{0.5}$ (33.3 at.% Mn, 50 at.% Cu, 16.7 at.% Ge) [1961Gla], for $Mn_{1.8}Cu_3Ge$ (31.0 at.% Mn, 51.7 at.% Cu, 17.3 at.% Ge) [1986Zav]
$τ_2$, $MnCu_2Ge$	t**	-	c/a = 0.96 [1963Oxl]
$τ_3$, $Mn_{33}Cu_{42}Ge_{25}$	-	-	[1987Zav]
$τ_4$, $Mn_{66}Cu_4Ge_{30}$	-	-	[1987Zav]
$τ_5$, $Mn_5(Cu_{0.133}Ge_{0.866})_3$	*tI*32 *I*4/*mcm* W_5Si_3	a = 955.9 ± 0.1 c = 491.8 ± 0.2	$Mn_{62.5}Cu_5Ge_{32.5}$ (62.5 at.% Ge, 5 at.% Cu, 32.5 at.% Ge) [1987Zav]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
τ_6, $(Mn_{0.8}Cu_{0.2})_3Ge_2$	*hP*6 $P6_3/mmc$ Ni_2In	a = 815 ± 4 c = 516 ± 1	in the alloy with 40 at.% Mn, 20 at.% Cu, 40 at.% Ge [1965Aoy],
		a = 816.9 ± 0.1 c = 515.6 ± 0.1	for $Mn_{48}Cu_{12}Ge_{40}$, single-phase (48 at.% Mn, 12 at.% Cu, 40 at.% Ge) [1987Zav]
τ_7, $(MnCu)_5Ge_2$	*hP*42 $P6_3cm$ Ni_5As_2	a = 718.5 to 715.5 c = 1306.5 to 1314	at 5 to 30 at.% Cu [1987Zav] Lattice parameters are taken from figure 3 in [1987Zav]

Table 3: Investigations of the Cu-Ge-Mn Materials Properties

Reference	Method/Experimental Technique	Type of Property
[1975Boc]	Bulk and film samples of Cu-(20 to 35) mass% Mn-(0.5 to 7.0) mass% Ge alloys. Measurements of electrical conductivity	Electrical conductivity at 25, 125 and 196°C
[1977Pop]	Bulk and film samples of Cu-(2.0 to 36) mass% Mn-(0.5 to 7.0) mass% Ge alloys. X-ray analysis	The phase analysis of films
[1978Nes]	The films of Cu-9 % Ge-(0.5 to 4 % Mn (mass) alloys. Effusion method, using open crucibles as effusion chambers.	The dependence of the rate evaporation and the partial vapor pressure from the alloy constitutions.
[1981Vin]	The layer of Cu-(0 to8) at.% Ge-(65 to 70) at.% Mn. Neutron and X-ray diffraction	The structural investigations
[1984Boc]	Bulk and film samples of Cu-(2.0 to 15) mass% Mn-(0.5 to 2.0) mass% Ge alloys	Electrical resistivity at 25 and 125°C.
[1985Dri2]	Bulk and film samples of Cu-2.0 mass% Mn-(0 to 15.0) mass% Ge alloys. Measurements of electrical resistivity of standard four-probe method. Auger spectroscopy.	Electrical resistivity at 25 and 125°C. The structural investigations of film surfaces.
[1990Boc]	Bulk and film samples of Cu-(0 to 15) mass% Mn-(0 to 15) mass% Ge alloys. X-ray analysis, Auger spectroscopy, measurement of electrical resistivity	Electrical resistivity at 25 and 125°C. The structural investigations of film surfaces.

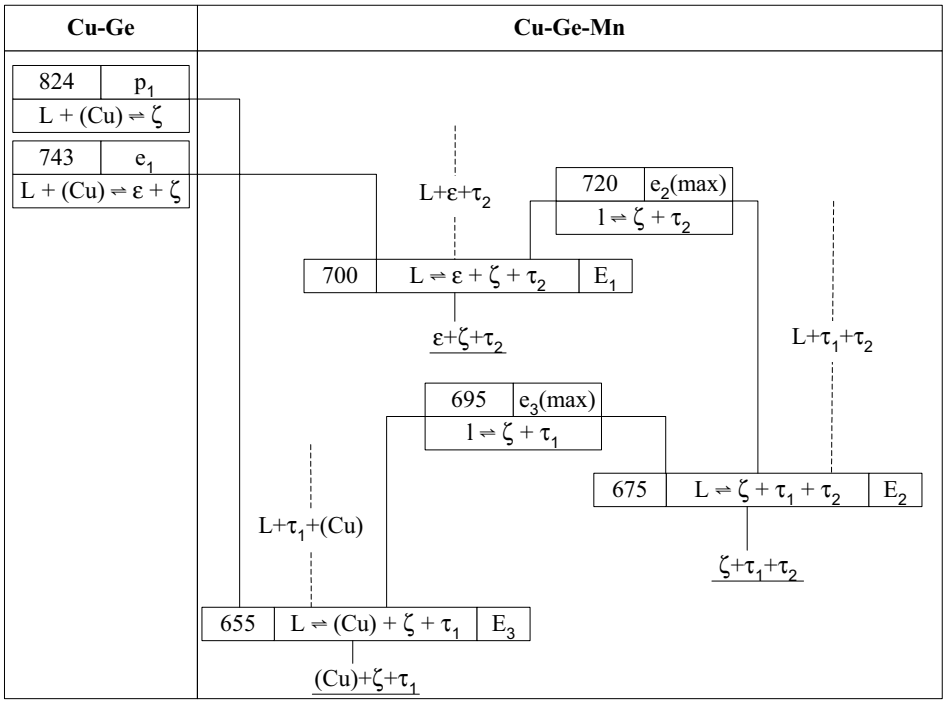

Fig. 1: Cu-Ge-Mn. Reaction scheme in the Cu corner

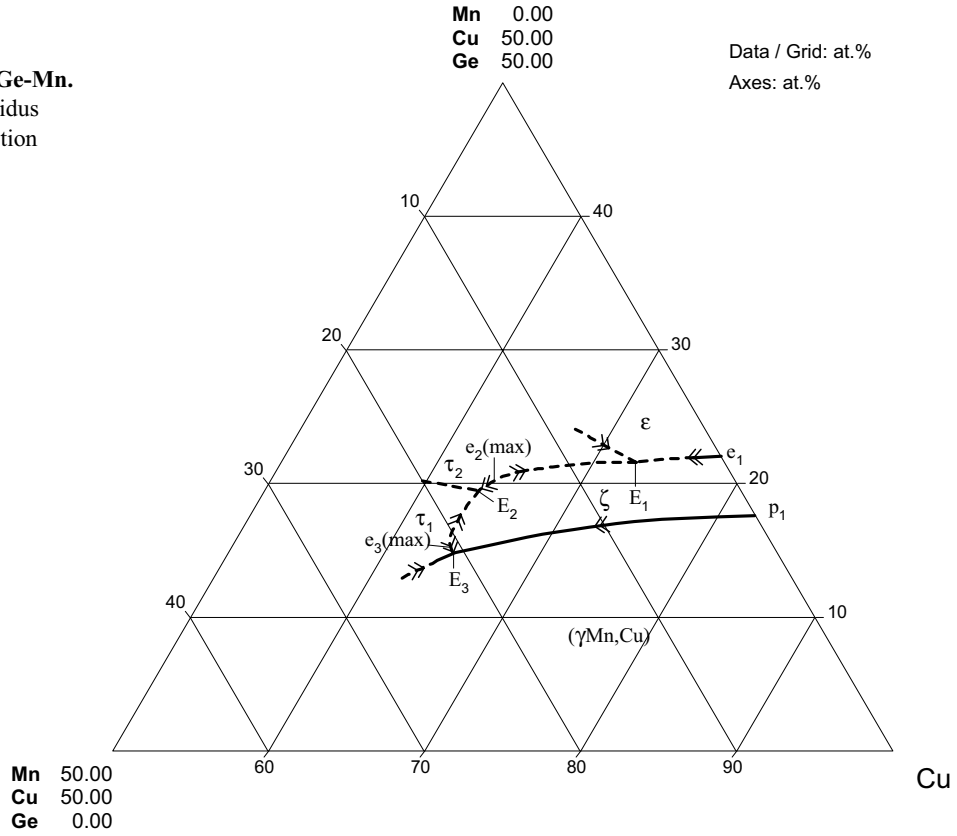

Fig. 2: Cu-Ge-Mn. Tentative liquidus surface projection

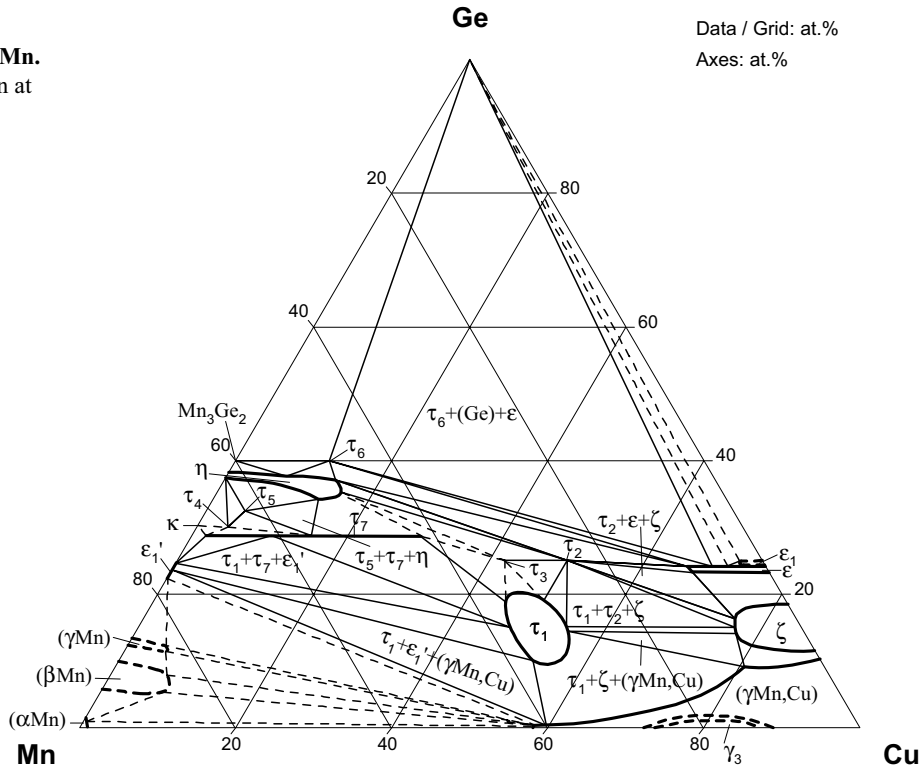

Fig. 3: Cu-Ge-Mn. Isothermal section at 600°C

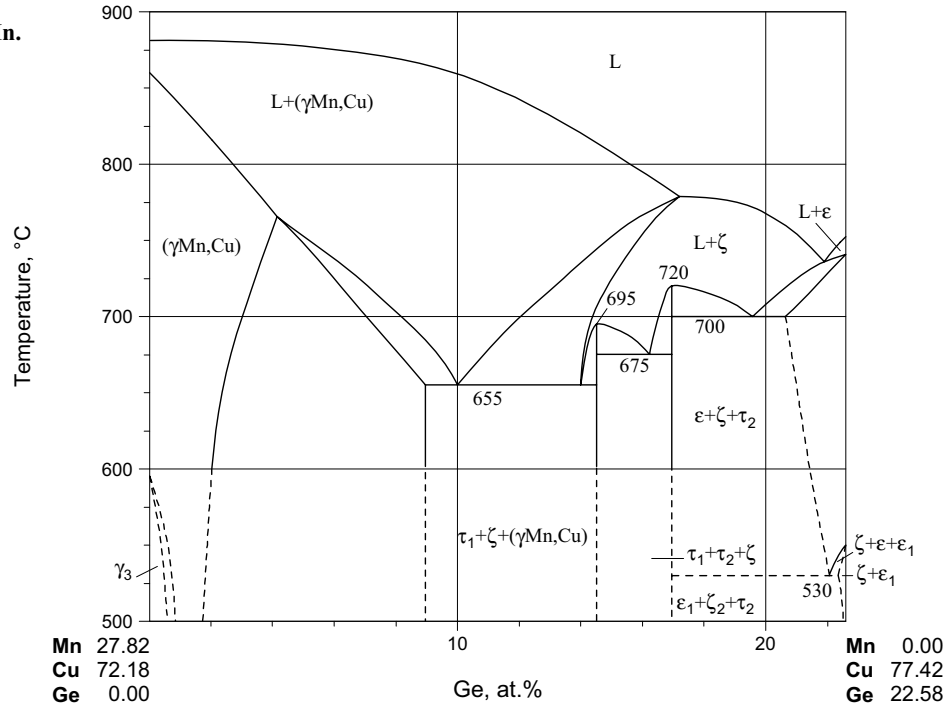

Fig. 4: Cu-Ge-Mn. Vertical section between binary compositions Cu-27.82Mn and Cu-22.58Ge (at.%)

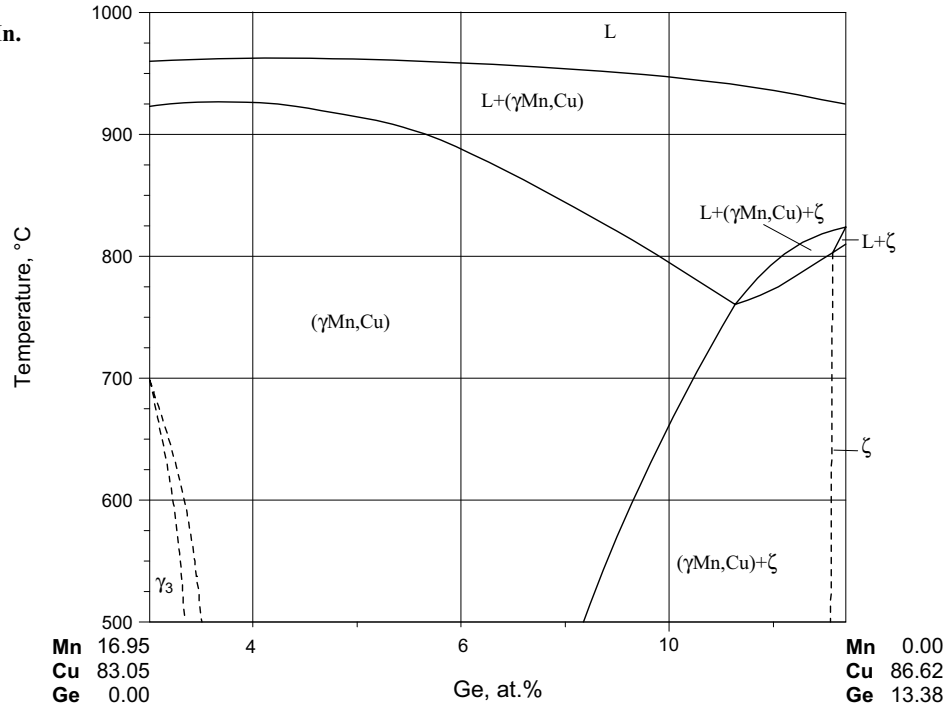

Fig. 5: Cu-Ge-Mn. Vertical section bewen binary compositions Cu-16.95Mn and Cu-13.38Ge (at.%)