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The Co-Ga-Ge (Cobalt-Gallium-Germanium) System

K.P. Gupta, The Indian Institute of Metals

An isothermal section of the Co-Ga-Ge has been established. Several ternary intermediate phases exist in the Co-Ga-Ge system.

Binary Systems

The Co-Ga system [Massalski2] (Fig. 1) has two intermediate phases: CoGa (β) and $CoGa_3$ (ν). Both these phases form through peritectic reactions L + (γCo) ↔ β at 1210 °C and L + β ↔ ν at 855 °C. A peritectic reaction L + ν ↔ (Ga) probably occurs very close to the Ga end at ~30.5 °C.

The Co-Ge system [Massalski2] (Fig. 2) has seven intermediate phases: Co_3Ge, Co_5Ge_2, βCo_5Ge_3 (δ), αCo_5Ge_3, CoGe, Co_5Ge_7, and $CoGe_2$. The βCo_5Ge_3 (δ) phase (earlier called the Co_2Ge phase) melts congruently at 1210 °C. At the Co end, the low-temperature cph (εCo) phase is stabilized by Ge and a peritectic reaction L + (γCo) ↔ (εCo) occurs at 1125 °C. The CoGe and $CoGe_2$ phases form through peritectic reactions: L + βCo_5Ge_3 ↔ CoGe at 985 °C and L + CoGe ↔ $CoGe_2$ at 832 °C. The Co_3Ge, Co_5Ge_7, and Co_5Ge_2 phases form through peritectoid reactions: (εCo) + βCo_5Ge_3 ↔ Co_3Ge at ~770 °C, CoGe + $CoGe_2$ ↔ Co_5Ge_7 at 808 °C, and (εCo) + βCo_5Ge_3 ↔ Co_5Ge_2 at 636 °C. Two eutectic reactions L ↔ (εCo) + βCo_5Ge_3 and L ↔ $CoGe_2$ + (Ge) occur at 1208 and 817 °C, respectively. The Co_3Ge and Co_5Ge_2 phases decompose through eutectoid reactions, Co_3Ge ↔ (εCo) + βCo_5Ge and Co_5Ge ↔ (εCo) + βCo_5Ge_3 at ~645 and 362 °C, respectively. The βCo_5Ge_3 phase transforms to the αCo_5Ge_3 phase below 385 °C.

The Ga-Ge system (Fig. 3) [Massalski2] is a simple eutectic system; the eutectic reaction L ↔ (Ga) + (Ge) is shown at the Ga end at 29.77 °C.

Binary and Ternary Phases

Eight intermediate phases form in the three binary systems. In the Co-Ga-Ge system, the existence of four ternary intermediate phases has been reported. The structure data of the binary and ternary phases of the Co-Ga-Ge system are given in Table 1.

Ternary System

In an exploratory study of the NiAs-related phases, [1957Ess] studied several binary and ternary alloys of the Co-Ga-Ge system. A CoGa alloy annealed at 420 °C showed the phase to be a CsCl-type structure with lattice parameter $a = 0.2866$ nm, which is slightly smaller than the value given in Table 1. Three ternary alloys of compositions $Co_{50}Ga_{37.5}Ge_{12.5}$, $Co_{50}Ga_{25}Ge_{25}$, and $Co_{50}Ga_{12.5}Ge_{37.5}$

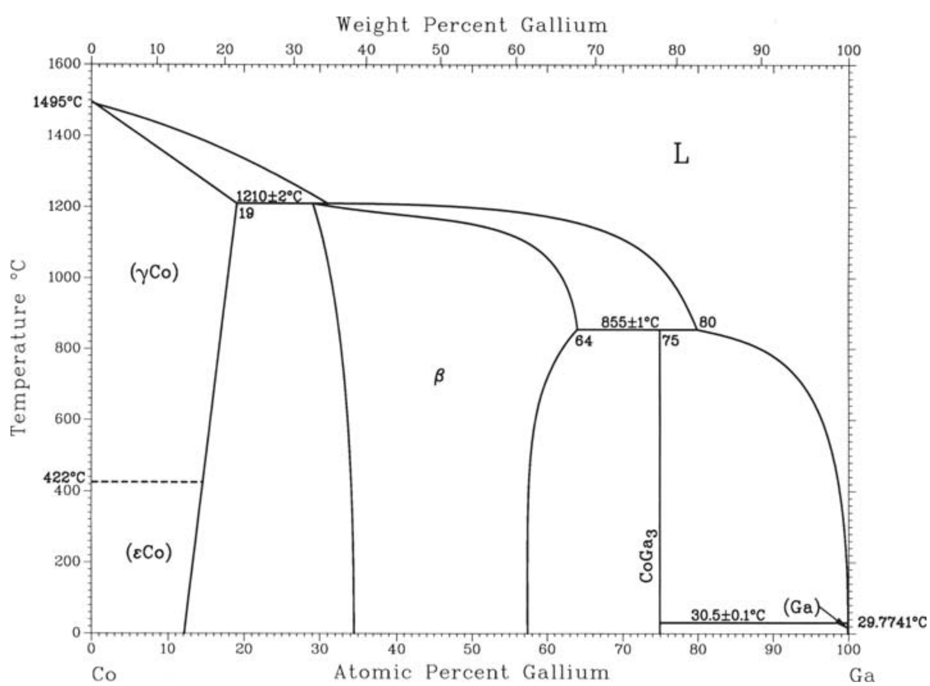

Fig. 1 Co-Ga binary phase diagram [Massalski2]

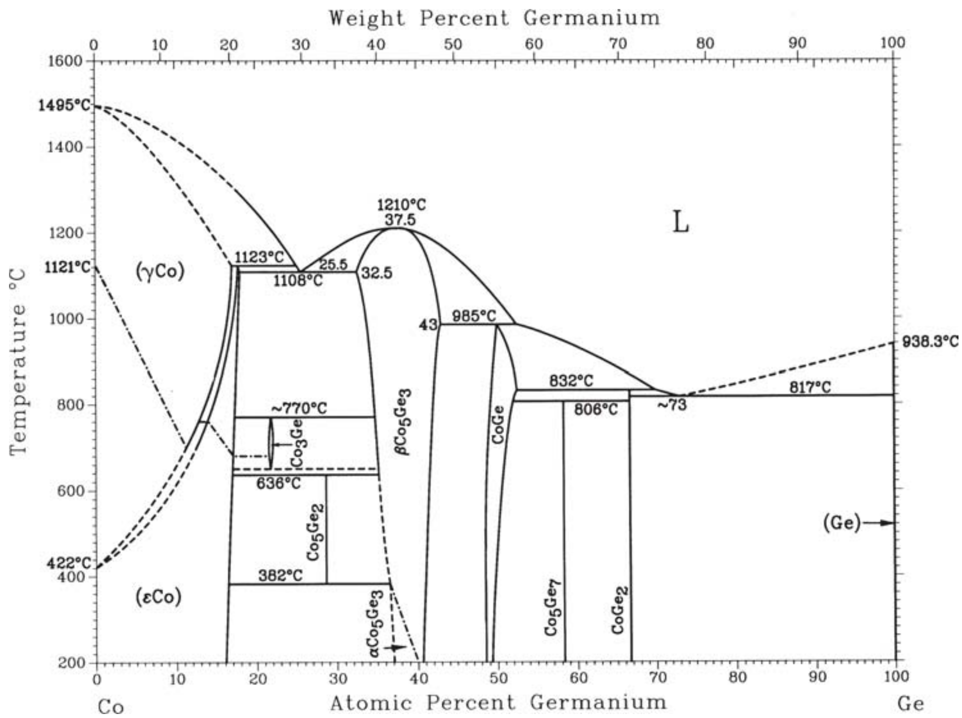

Fig. 2 Co-Ge binary phase diagram [Massalski2]

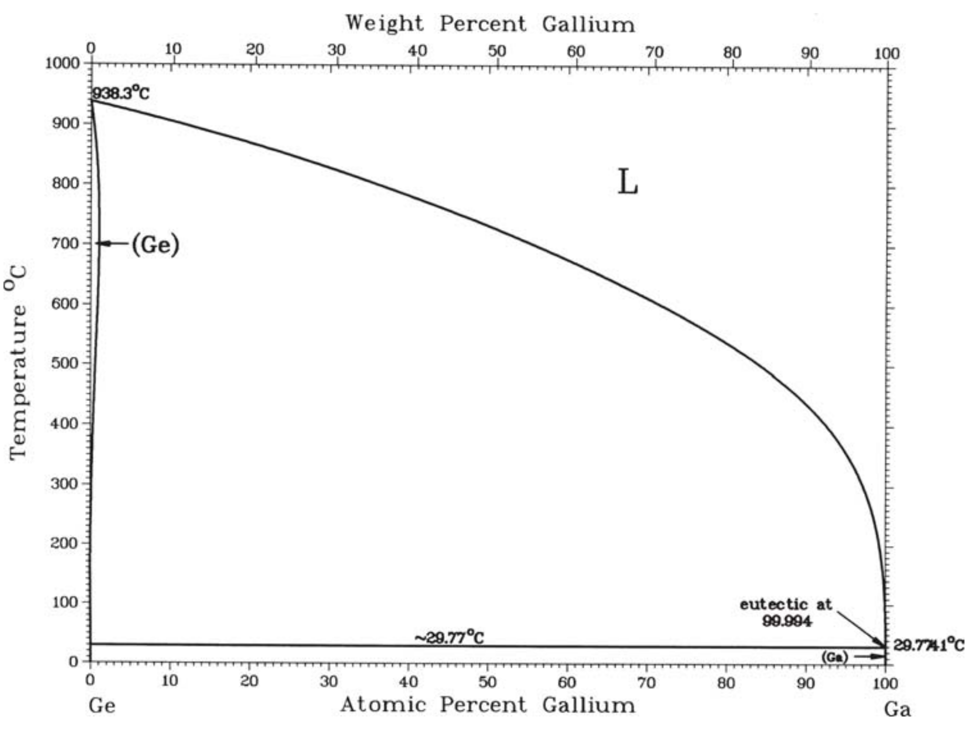

Fig. 3 Ga-Ge binary phase diagram [Massalski2]

were annealed at 500 °C for 12 h. The 12.5 at.% Ge alloy was found to have two phases, predominantly consisting of CoGa, β phase and a second phase having lattice parameters $a = 0.5010$ nm and $c = 0.4043$ nm. The composition of the second phase, however, was not given. The alloy with 25 at.% Ge was found to have three phases: CoGa + a phase with composition Co_4GaGe_3 + a third phase that was not identified. The lattice parameters of the FeSi-type Co_4GaGe_3, (Λ) phase was found to be $a = 0.4639$ nm. The alloy with 37.5 at.% Ge was found to have two phases containing predominantly Λ phase (~90%) with a second phase, which was tentatively identified as a NiAs-related phase.

A more detailed investigation of the Co-Ga-Ge system was done by [1969Pan]. The alloys were arc melted under an argon atmosphere with component elements of >99.5 mass% purity. The alloys were annealed at 750 °C for 12 h in evacuated and sealed quartz capsules. The powder x-ray diffraction method was used for phase identification. An isothermal section at 750 °C was established and is given in Fig. 4.

In addition to the ternary intermediate phase Co_4GaGe_3 (Λ) earlier identified by [1957Ess], Fig. 4 shows the presence of two other ternary intermediate phases: Φ ($Co_{36}Ga_{37}Ge_{27}$) and Σ ($Co_3Ga_2Ge_5$). The βCo_5Ge_3 phase (δ) was found to extend to about 20 at.% Ga. The CoGa phase (β) was found to extend to ~35 at.% Ge. The Φ phase was found to exist very close to the intrusive β Co(Ga,Ge) phase. The β phase was found in equilibrium with the (γCo), β Co_5Ge_3 (δ), Λ, Φ, Σ, (Ge), and $CoGe_3$ (ν) phases. The Λ phase was found to extend along the 50 at.% Co line from about 28 at.% Ge to about 43 at.% Ge and was found in equilibrium with the δ, CoGe (ρ), Co_5Ge_7 (ζ), Σ, and Φ phases. The Σ phase extended along a 30 at.% Co line from about 44 at.% Ge to about 52 at.% Ge and was found in equilibrium with the Φ, Λ, ρ, ζ, $CoGe_2$ (ι), (Ge), and β phases. A three-phase equilibrium region (Ge) + (Ga) + ν was also indicated.

To determine the structure of the low-temperature form of Co_2Ge phase (αCo_5Ge_3 phase) [1969Pan] used an alloy of composition $Co_{67}Ge_{33}$ that was annealed at 550 °C and then cooled in air. Analysis of the powder diffraction pattern of this alloy showed it to have a Ni_2Si-type structure with lattice parameters a = 0.726 nm, b = 0.502 nm, and c = 0.382 nm.

The 750 °C isothermal section of the Co-Ga-Ge system [1969Pan] appears incomplete on the basis of the accepted binary phase diagrams. Since the (ϵ Co) phase exists at 750 °C in the Co-Ge system, two three-phase equilibrium regions (γCo) + (ϵCo) + β′ and (ϵCo) + β′ + δ should exist

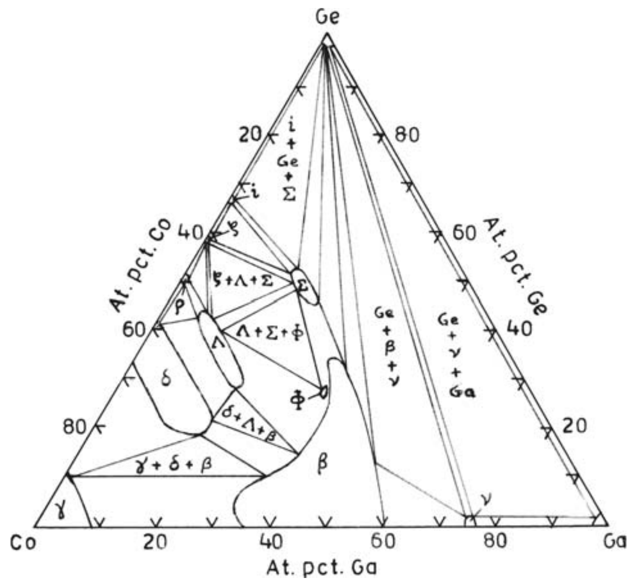

Fig. 4 A 750 °C isothermal section of the Co-Ga-Ge system [1969 Pan]

Table 1 Binary and ternary phases of the Co-Ga-Ge system and their structure data

Phase designations	Composition	Pearson symbol	Space group	Type	Lattice parameters, nm		
					a	*b*	*c*
γ	(γCo)	*cF*4	$Fm\bar{3}m$	Cu	…	…	…
ϵ	(ϵCo)	*hP*2	$P6_3/mmc$	Mg	…	…	…
Ga	(Ga)	*oC*6	*Cmca*	αGa	…	…	…
Ge	(Ge)	*cF*8	$Fd\bar{3}m$	C(diamond)	…	…	…
β	CoGa	*cP*2	$Pm\bar{3}m$	CsCl	0.2878	…	…
ν	$CoGa_3$	*tP*16	$P4_2/mnm$	$CoGa_3$	0.62365	…	0.64347
ξ	Co_4Ge	…	…	…	…	…	…
β′	Co_3Ge	*cP*8	$Pm\bar{3}n$	Cr_3Si	…	…	…
θ′	Co_5Ge_2	…	…	…	…	…	…
δ	βCo_5Ge_3(a)	*hP*6	$P6_3/mmc$	$InNi_2$	0.3933	…	0.5014
δ′	αCo_5Ge_3	*oP*12	*Pbnm*	Ni_2Si	0.726(b)	0.502(b)	0.382(b)
ρ	CoGe	*mC*16	*C*2/*m*	CoGe	1.1648	0.3807	0.4945
		*cP*8	$P2_13$	FeSi	…	…	…
ζ	Co_5Ge_7	*tI*24	*I*4/*mm*	Co_5Ge_7	0.764	…	0.581
ι	$CoGe_2$	*oC*24	*Aba*2	$PdSn_2$	0.5681	0.5681	1.0818
Λ	Co_4GaGe_3	*cP*8	$P2_13$	FeSi	0.4639	…	…
Φ	$Co_{36}Ga_{37}Ge_{27}$	…	$C\bar{3}m$	Ni_2Al_3	0.401	…	0.483
Σ	$Co_3Ga_2Ge_5$	…	$Im\bar{3}m$	Ru_3Sn_7	0.8395	…	…
Γ	Co_6GaGe_3(c)	…	…	$Pd_{13}Tl_9$	0.783	…	0.496

(a) The βCo_5Ge_3 in earlier literature is referred to as the Co_2Ge(H) phase. (b) Lattice parameter from [1969Pan]. (c) The Γ phase exists as a stable phase at 1000 °C, but does not exist at 750 °c.

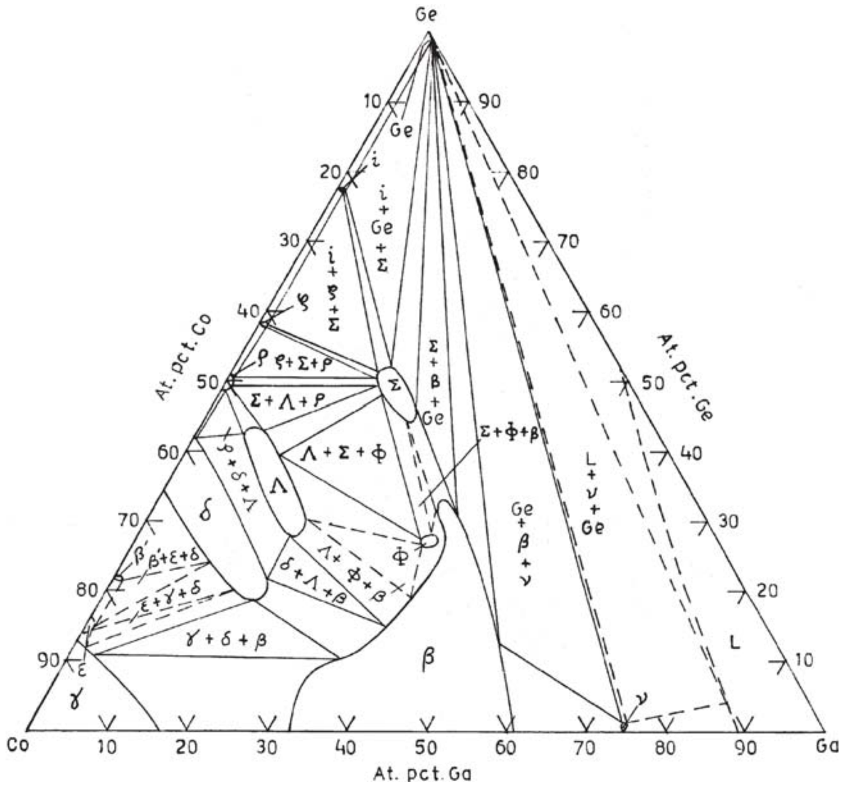

Fig. 5 A probable 750 °C isothermal section (schematic) of the Co-Ga-Ge system

in the Co-Ga-Ge system. At 750 °C, Ga is in liquid state and hence a liquid region should exist at the Ga end and a three-phase equilibrium region ν + L + (Ge) should be present instead of a solid (Ga) + L + ν phase three-phase region. The phase equilibrium involving the Φ phase is also incomplete in Fig. 4. Two three-phase equilibrium regions Λ + Φ + β and Φ + β + Σ should also exist. A probable 750 °C isothermal section showing schematically the expected phase regions and the three-phase equilibrium triangles (shown with dashed lines) is given in Fig. 5.

The results of [1969Pan] at 750 °C and of [1957Ess] at 500 °C, however, suggest phase equilibria in the Co-Ga-Ge system to be somewhat different at the two temperatures. While [1969Pan] showed that the alloy of composition $Co_{50}Ga_{12.5}Ge_{37.5}$ lies in the Λ phase region at 750 °C, the same alloy at 500 °C [1957Ess] has two phases, ~90% Λ + a phase related to the NiAs phase. Since the NiAs-related δ phase has been found in equilibrium with the Λ phase at 750 °C, it is possible that the observed NiAs-related phase at 500 °C is the δ phase. Thus it appears that the Λ phase region is smaller and does not extend beyond ~35 at.% Ge at 500 °C. Moreover, the phase with lattice parameters a = 0.5010 nm and c = 0.4043 nm, observed in the alloy containing 50 at.% Co, 37.5 at.% Ga, and 12.5 at.% Ge at 500 °C [1957Ess], was not found by [1969Pan] at 750 °C.

[1969Pan] annealed an alloy of composition $Co_{60}Ga_{10}Ge_{30}$, which is single-phase δ at 750 °C, at 1000 °C for 8 h, and observed that a new phase Γ exists at 1000 °C. The Γ phase was identified to be a $Pd_{13}Tl_9$-type phase with lattice parameters a = 0.783 nm and c = 0.496 nm. All these results indicate that the phase equilibria in Co-Ga-Ge system at temperatures higher and lower than 750 °C is possibly significantly different than established by [1969Pan] at 750 °C. Further work will thus be necessary to study phase equilibria in the Co-Ga-Ge system at various temperatures above and below 750 °C.

References

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*Indicates key paper.
#Indicates presence of a phase diagram.

Co-Ga-Ge evaluation contributed by **K.P. Gupta,** The Indian Institute of Metals, Metal House, Plot 13/4, Block AQ, Sector V, Calcutta, India. Literature searched through 1997. Dr. Gupta is the Alloy Phase Diagram Co-Category Program Editor for ternary alloys.