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The Ga-Ge-Ni (Gallium-Germanium-Nickel) System

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Introduction

The Ga-Ge-Ni system was investigated at only one temperature. A partial isothermal section was established in the Ga-Ge-Ni system. A large number of ternary intermediate phases exist in the investigated region of the Ga-Ge-Ni system.

Binary Systems

The Ga-Ni system [1991Nas] (Fig. 1) shows the presence of seven intermediate phases: $GaNi_3$ (β), Ga_3Ni_5 (δ′), Ga_2Ni_3 (ε), GaNi (ν), Ga_4Ni_3 (θ), Ga_3Ni_2 (β′), and Ga_4Ni (ρ). The Ga_2Ni_3 phase has an allotropic form γ′ at < 680 °C. The GaNi phase melts congruently at 1220 °C at ~35 at.% Ga. The $GaNi_3$ (β), Ga_3Ni_2 (β′), and Ga_4Ni (ρ) phases form through peritectic reactions: L + γ ↔ β, at 1212 °C, L + ν ↔ β′ at 895 °C, and L + β′ ↔ ρ at 363 °C, where γ is the face-centered-cubic (fcc) terminal solid solution of Ga in Ni. Possibly a peritectic reaction L + ρ ↔ (Ga) occurs at ~30 °C. A eutectic reaction L ↔ β + ν occurs at 1207 °C. The δ′, ε, and θ phases form through peritectoid reactions ν + β ↔ ε at 949 °C, ε + β ↔ δ′ at 741 °C, and ν + β′ ↔ θ at 542 °C.

The Ga-Ge system [Massalski2] (Fig. 2) is a simple eutectic system with L ↔ (Ge) + (Ga) reaction occurring close to Ga at ~29.77 °C.

The Ge-Ni system [1991Nas] (Fig. 3) has nine intermediate phases: $\beta GeNi_3$ (β), $\gamma' GeNi_3$ (α′), δGe_2Ni_5 (δ), $GeNi_2$ (π), εGe_3Ni_5 (ε), $\varepsilon' Ge_3Ni_5$ (ε′), $Ge_{12}Ni_{19}$ (ζ), Ge_2Ni_3 (ξ), and GeNi (ι) of which the β and ε phases melt congruently at 1132 and 1185 °C, respectively. The ε ↔ ε′ transformation occurs congruently at ~398 °C. The γ, δ, ζ, ξ, and ι phases form through peritectic reactions: L + β ↔ γ at 1118 °C, L + α ↔ δ at 1102 °C, L + ε ↔ ζ at 1050 °C, L + ζ ↔ ξ at 990 °C, and L + ξ ↔ ι at 850 °C. The π phase forms through a peritectoid reaction β + ε ↔ π at 506 °C. Three eutectic reactions L ↔ α + β, L ↔ δ + ε, and L ↔ ι + (Ge) occur at 1124, 1099, and 762 °C, respectively. The γ and δ phases exist only at high temperatures and undergo eutectoid transformation γ ↔ β + δ and δ ↔ β + ε at 1082 and 1045 °C, respectively. The ζ, ξ, and ε phases undergo four eutectoid transformations: ξ ↔ ζ + ι, ε ↔ ε′ + ζ, ζ ↔ ε′ + ι, and ε ↔ π + ε′ at 515, ~394, 382, and 290 °C, respectively.

Binary and Ternary Phases

The three binary systems of the Ga-Ge-Ni system have sixteen intermediate phases with one of the phases in the

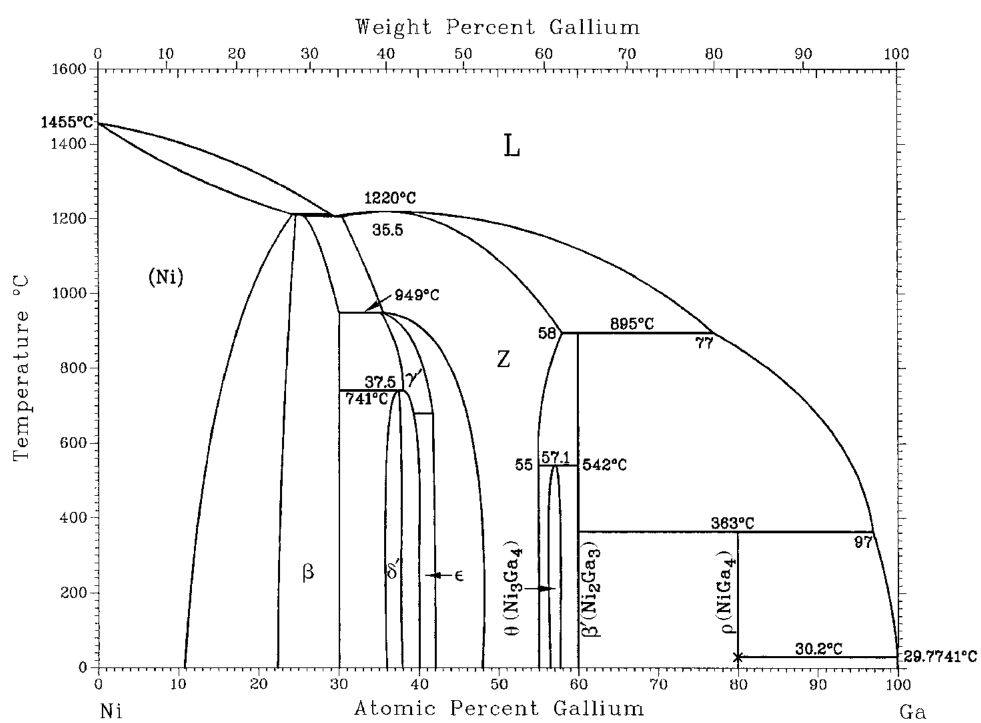

Fig. 1 Ga-Ni binary phase diagram [1991Nas]

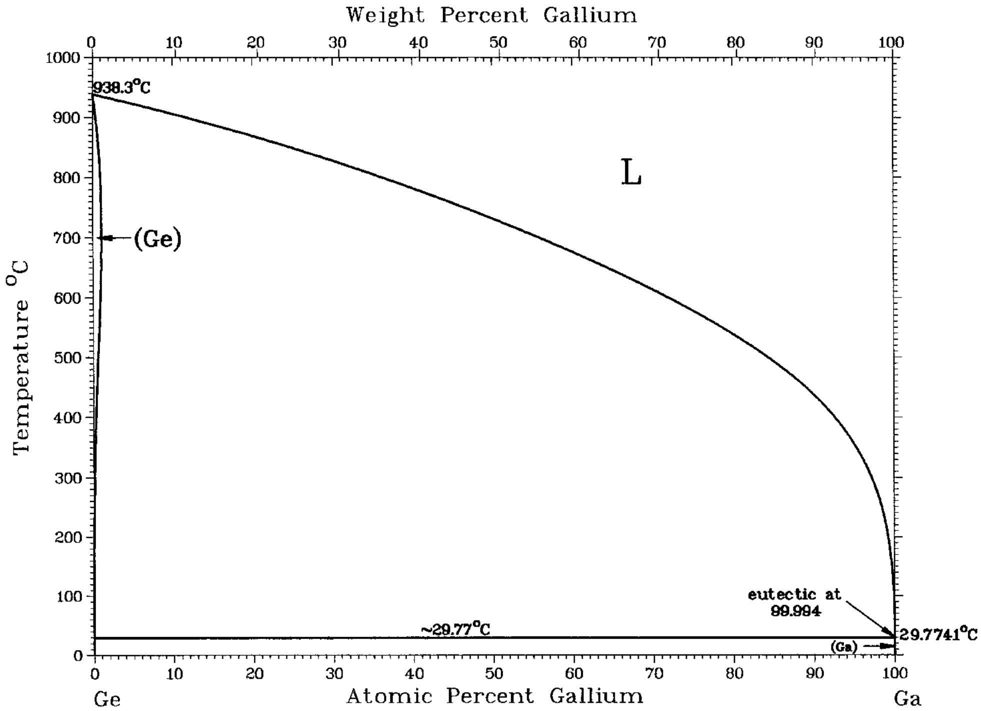

Fig. 2 Ga-Ge binary phase diagram [Massalski2]

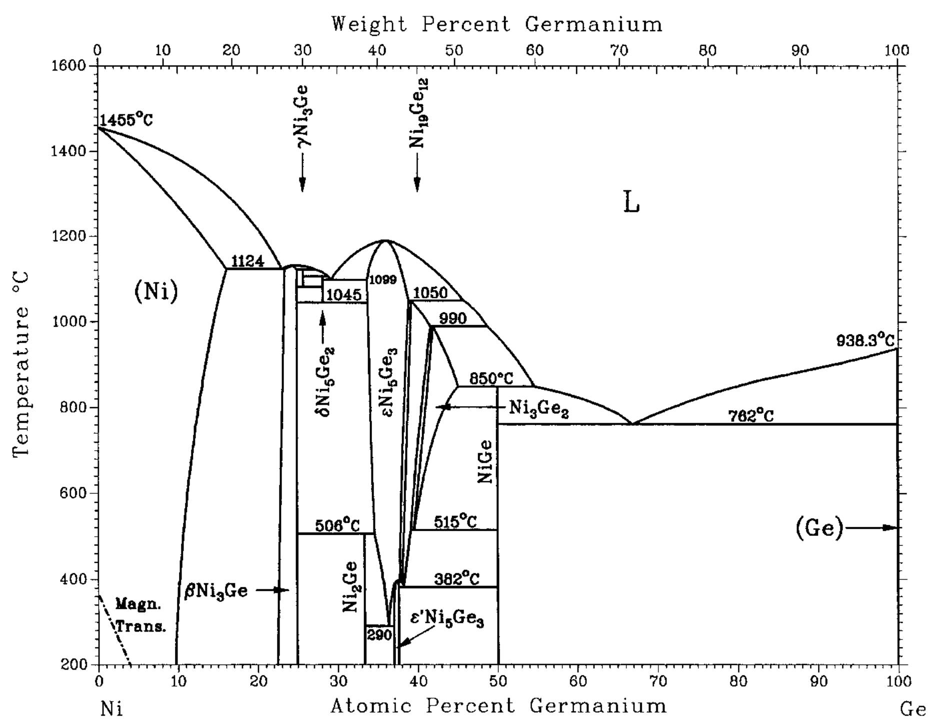

Fig. 3 Ge-Ni binary phase diagram [1991Nas]

Ga-Ni system having an allotropic form at lower temperature. The investigated region of the Ga-Ge-Ni system has seven intermediate phases. The phases and their structure data are given in Table 1.

Ternary System

In an exploratory work on T-β^3-β^4 systems, where T = Mn, Fe Co, Ir, Ni, and Pd, β^3 = Al and Ga, and β^4 = Si and Ge, [1969Pan] studied the Ga-Ge-Ni system. To pre-

Table 1 Phase present in Ga-Ge-Ni ternary system and their structure data

Phase designation	Composition	Pearson's symbol	Space group	Type	Lattice parameters, nm		
					a	*b*	*c*
(Ga)	(Ga)	*oC*8	*Cmca*	αGa	…	…	…
(Ge)	(Ge)	*cF*8	$Fd\overline{3}m$	C(diamond)	…	…	…
(Ni)	(Ni)	*cF*4	$Fm\overline{3}m$	Cu	…	…	…
β	$GaNi_3$	*cP*4	$Pm\overline{3}m$	$AuCu_3$	0.35850	…	…
ν	GaNi	*cP*2	$Pm\overline{3}m$	Cscl	0.2873	…	…
ε	Ga_2Ni_3	*hP*4	$P6_3/mmc$	AsNi	0.3995	…	0.4980
α′	Ga_2Ni_3	…	…	…	1.3785	0.7883	0.8457
						β = 35.9°	
δ′	Ga_3Ni_5	*oC*16	*Cmcm*	Ga_3Pt_5	0.376	…	0.339
θ	Ga_4Ni_3	*cI*112	*Ia*3*d*	Ga_4Ni_3	1.141	…	…
β′	Ga_3Ni_2	*hP*5	$P\overline{3}m1$	Al_3Ni_2	0.405	…	0.489
ρ	Ga_4Ni	*cI*52	$I\overline{4}3m$	Cu_5Zn_8	0.8406	…	…
β	$\beta GeNi_3$	*cP*4	$Pm\overline{3}m$	$AuCu_3$	0.357	…	…
α′	$\alpha' GeNi_3$	…	…	…	…	…	…
δ	δGe_2Ni_5	*hP*84	$P6_3/mmc$	Pd_5Sb_2	0.6827	…	1.2395
π	$GeNi_2$	*oP*12	*Pnma*	Co_2Si	0.7264	0.511	0.383
ε′	$\varepsilon' Ge_3Ni_5$	*mC*32	*C*2	Ge_3Ni_5	1.1682	0.6737	0.6364
						β = 52.1°	
ε	εGe_3Ni_5	*hP*4	$P6_3/mmc$	AsNi	0.3955	…	0.5047
ζ	$Ge_{12}Ni_{19}$	*mC*62	*C*2	$Ge_{12}Ni_{19}$	1.1631	0.6715	1.0048
						β = 90°	
ξ	Ge_2Ni_3	*nP*4	$P6_3/mmc$	AsNi	0.386	…	0.500
ι	GeNi	*oP*8	*Pnma*	MnP	0.581	0.538	0.343
Φ	$GaGe_3Ni_2$	…	*Bba*	$CoGe_2$	0.5725	0.5725	1.0815(a)
Λ	$GaGe_7Ni_8$	…	*C*2/*m*	CoGe	1.1618	0.3784	0.4904(a)
						β = 102.49°	
Δ	$Ga_3Ge^{\circ}Ni_4$	*c*	$P2_13$	FeSi	…	…	…
Σ	$GaGe_2Ni_4$	*h*	…	Superstructure related to AsNi	0.783	…	1.5005(b)
Ψ	$GaGeNi_2$	…	…	…	…	…	…
Ω	$GaGeNi_3$	*o*	…	Superstructure related to AsNi	0.7909	1.3665	2.0023(b)
Γ	$GaGe_3Ni_4$	…	*Pnma*	$GaGe_3Ni_4$	0.4934	0.3844	1.1412(a)

(a) Lattice paraemeters from [1969Pan]. (b) Lattice parameters from [1973Ell]

pare the alloys >99.5 mass% pure component elements were arc melted under an argon atmosphere. The alloys were homogenized in sealed quartz capsules, and temperature and time for homogenization were not mentioned. Powder specimens for x-ray diffraction (XRD) were annealed at 700 °C for 12 to 48 h in sealed quartz capsules and water quenched. XRD was used for phase identification and the Weissenberg single crystal method was used for structure determination of a few ternary intermediate phases. Besides the Ga_3GeNi_4 phase (Δ), which was earlier reported by [1957EBl], existence in the Ga-Ge-Ni system of five new ternary phases were found. For three of these phases, $GaGe_3Ni_2$ (Φ), $GaGe_7Ni_8$ (Λ), and $GaGe_3Ni_4$ (Γ), crystal structures were determined. Crystal structure determinations have not been reported for the other three ternary phases, Σ, Ψ, and Ω. Two of these, Ψ and Ω, had previously been reported by [1969Pan] who had designated them X and Y. The studies of [1969Pan] were the basis of a proposal for a tentative partial ternary phase diagram, which showed the approximate locations of these two ternary phases.

[1973Ell] made a more complete investigation of the Ga-Ge-Ni system. In this investigation >99.9 mass% pure elements were used for arc melting of alloys, and the alloys were homogenized at 700 °C for 12 h. The alloys were then annealed at 700 °C for 24 to 48 h and characterized using metallography, XRD with crystal structures of a few phases being determined by the Weissenberg single crystal method. [1973Ell] reported the presence of seven ternary intermediate phases in the Ga-Ge-Ni system, including the phases reported earlier by [1957Lin] and [1969Pan]. Two isostructural phases of the Ga-Ni and Ge-Ni systems, namely the $GaNi_3$ and $GeNi_3$ (β phases) and the Ga_2Ni_3 and Ge_3Ni_5 (ε phases), were found to form two continuous series of solid solution phase regions at 700 °C. The X and Y phases of [1969Pan] were identified as the $GaGeNi_3$ (Ω) and $GaGeNi_2$ (Ψ), respectively. A ternary intermediate $GaGe_2Ni_4$ (Σ) was also identified, but its

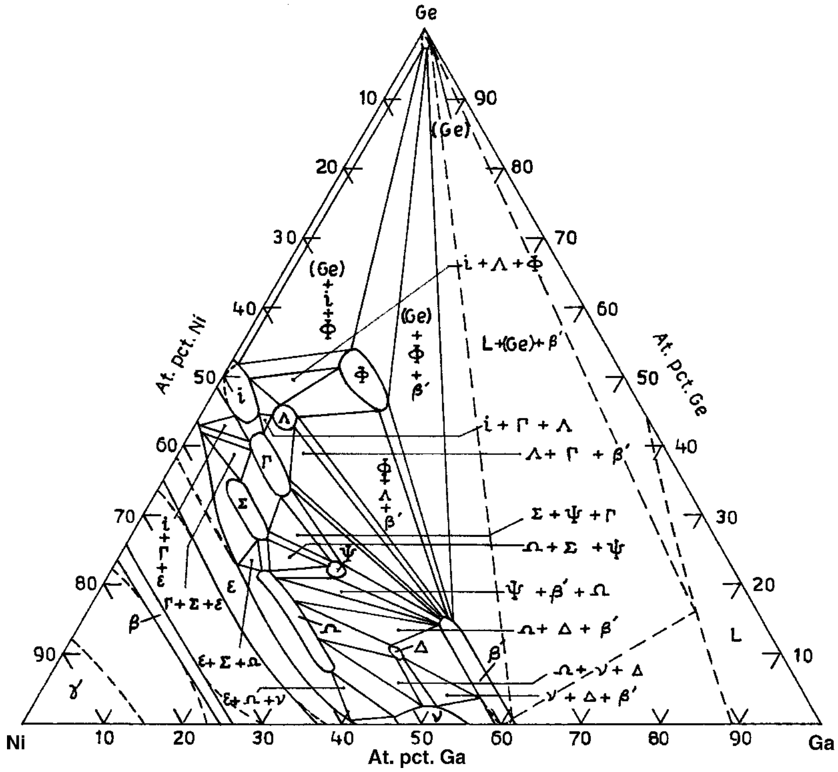

Fig. 4 The 700 °C isothermal section of the Ga-Ge-Ni system [1973Ell]. The dashed lines indicate probable boundaries of the phase regions.

crystal structure was not determined. The phase boundaries of all the phases were determined and a proposed phase equilibria for the Ga-Ge-Ni system at 700 °C is shown in Fig. 4.

Because of the concentration of [1973Ell]'s work in the Ni-rich region, the diagram in Fig. 4 is better defined on the high Ni side of the (Ge)-(Ga_2Ni_3) line and quite tentative on the Ga-rich side of that line. The fcc γ phase boundary was not determined by [1973Ell] and is shown schematically in Fig. 4 on the basis of the binary solid solubility data of Ga and Ge in Ni at 700 °C. The β and ε phase regions extend from the Ga-Ni binary to the Ge-Ni binary. The ε phase was found in equilibrium with the ν, Ω, Σ, Γ, and ι phases. The Δ phase was found in equilibrium with the ν, Ω, and β′ phases, and the Ψ phase was found in equilibrium with the β′, Ω, Σ, and Γ phases. The Λ phase was found in equilibrium with the β′, Γ, Φ, and ι phases, and the Φ phase was found in equilibrium with the ι, Λ, β′, and (Ge) phases. The β′ phase was also found in equilibrium with the (Ge) terminal solid solution phase. On the high Ga side of the β′-(Ge) line no investigation was carried out. From the binary data on Ga-Ni and Ga-Ge systems, it may be reasonable to assume the presence of a liquid region (L) at the Ga corner of the isothermal section at 700 °C. Schematically the liquid region is shown in Fig. 4. If no other intermediate phase exists in the (Ge)-β′-Ga region, then a wide three phase triangle L + β′ + (Ge) should exist in this region, which is also indicated in Fig. 4.

While the 700 °C isothermal section of the Ga-Ge-Ni (Fig. 4) appears to be well established; there remain certain discrepancies related to the phase boundaries of the binary phases β, ε, ι, and β′. The accepted Ga-Ni and Ge-Ni binary

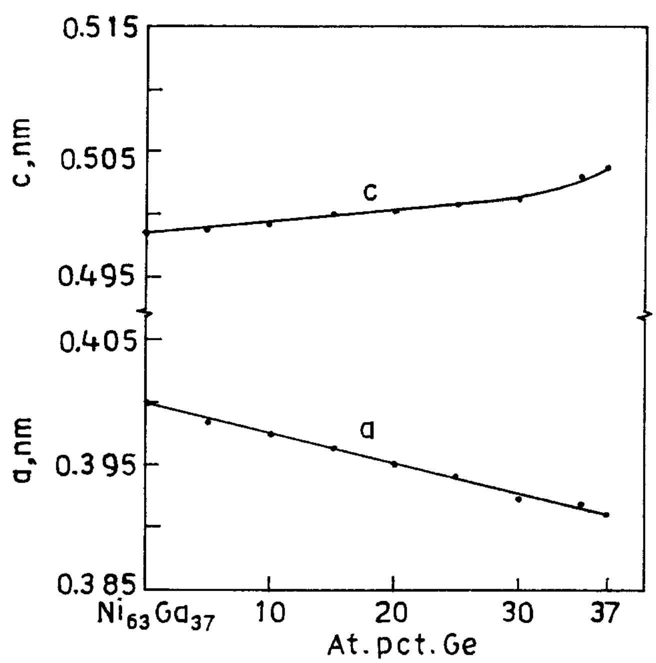

Fig. 5 Variation of lattice parameters of the ε phase along the $Ga_{37}Ni_{63}$-$Ge_{37}Ni_{63}$ line as a function of Ge content

diagrams indicate the ι and β′ phases to be of invariant composition, whereas they are shown in Fig. 4 with reasonably wide phase regions. The β phase region is somewhat wider on the Ga-Ni side, whereas the ε phase region at the Ge-Ni binary limit is comparatively narrow compared to what is shown in Fig. 4. The probable phase boundaries of the β, ε, ι, and β′ phases are indicated in Fig. 4 by dashed lines. The β, ε, ι, and β′ phase boundaries as well as some of the three phase equilibrium triangles involving these phases should be redetermined.

[1976Ell] reported the lattice parameters of the ε phase alloys along the $Ga_{37}Ni_{63}$-$Ge_{37}Ni_{63}$ line as a function of Ge content (Fig. 5). The lattice parameters of the ε phase were found to vary linearly with Ge content over most of the composition but with the ***c*** parameter developing a slight curve near the Ni-Ge binary boundary.

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#Indicates presence of phase diagram.

Ga-Ge-Ni 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 1993. Dr. Gupta is the Alloy Phase Diagram Program Co-Category Editor for ternary nickel alloys.