Co – Ge (Cobalt – Germanium)

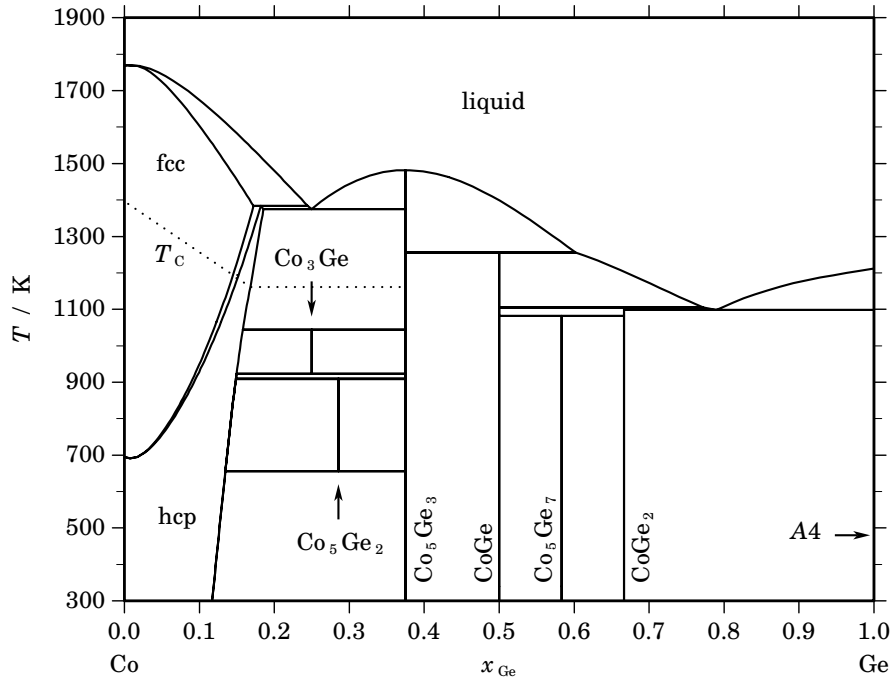

Fig. 1. Calculated phase diagram for the system Co-Ge.

The equilibrium phases are the liquid, the Co-rich fcc solid solution, the Co-rich hcp solid solution, the Ge-rich solid solution, with negligible solid solubility of Co and 6 near-stoichiometric compounds Co_3Ge, Co_5Ge_2, Co_5Ge_3, CoGe, Co_5Ge_7 and $CoGe_2$. Two compounds, CoGe and $CoGe_2$, decompose peritectically at 1258 and 1105 K, respectively. CoGe has a narrow homogeneity range of about 2.5 at.% with a stoichiometric composition at the peritectic temperature. The compound Co_5Ge_7 is stable up to the peritectoid temperature of 1079 K. Co_3Ge is formed below about 1043 K, the hexagonal phase Co_5Ge_2 is stable between 655 and 909 K. The phase Co_5Ge_3 which exhibits a fairly wide homogeneity range of almost 10 at.% melts congruently at 1483 K. The thermodynamic assessment of the Co-Ge system carried out by Korb [2004Kor] is based on [1949Pfi, 1980Day, 1990Eno], with review of the data of [1952Kös, 1973Aga, 1976Bal]. All compounds have been treated as stoichiometric, including Co_5Ge_3 and CoGe. Taking into account this simplification the calculated and the published [1991Ish] phase diagram agree well.

Table I. Phases, structures and models.

Phase	Struktur-bericht	Prototype	Pearson symbol	Space group	SGTE name	Model
liquid					LIQUID	$(Co,Ge)_1$
fcc	$A1$	Cu	$cF4$	$Fm\overline{3}m$	FCC_A1	$(Co,Ge)_1$
hcp	$A3$	Mg	$hP2$	$P6_3/mmc$	HCP_A3	$(Co,Ge)_1$
Co_3Ge	$A15$ (?)	Cr_3Si (?)	$cP8$ (?)	$Pm\overline{3}n$ (?)	CO3GE	Co_3Ge_1
Co_5Ge_2	···	···	$hP*$	···	CO5GE2	Co_5Ge_2
αCo_5Ge_3	···	···	$oP*$	$Pbnm$?	CO5GE3	Co_5Ge_3
βCo_5Ge_3	$B8_2$	$InNi_2$	$hP6$	$P6_3/mmc$	CO5GE3	Co_5Ge_3
CoGe	···	···	$mC16$	$C2/m$	COGE	Co_1Ge_1
Co_5Ge_7	···	···	$tI24$	$I4mm$	CO5GE7	Co_5Ge_7
$CoGe_2$	···	···	$oC24$	$Aba2$	COGE2	Co_1Ge_2
$A4$	$A4$	C(diamond)	$cF8$	$Fd\overline{3}m$	DIAMOND_A4	Ge_1

Table II. Invariant reactions.

Reaction	Type	T / K	Compositions / x_{Ge}			$\Delta_r H$ / (J/mol)
liquid $\rightleftharpoons$ Co_5Ge_3	congruent	1481.9	0.375	0.375		−64617
fcc + liquid $\rightleftharpoons$ hcp	peritectic	1383.8	0.172	0.245	0.182	−6168
liquid $\rightleftharpoons$ hcp + Co_5Ge_3	eutectic	1374.7	0.250	0.186	0.375	−42156
Co_5Ge_3 + liquid $\rightleftharpoons$ CoGe	peritectic	1256.3	0.375	0.602	0.500	−32569
CoGe + liquid $\rightleftharpoons$ $CoGe_2$	peritectic	1105.1	0.500	0.772	0.667	−32166
liquid $\rightleftharpoons$ $CoGe_2$ + $A4$	eutectic	1098.1	0.790	0.667	1.000	−49871
CoGe + $CoGe_2$ $\rightleftharpoons$ Co_5Ge_7	peritectoid	1081.8	0.500	0.667	0.583	−1493
hcp + Co_5Ge_3 $\rightleftharpoons$ Co_3Ge	peritectoid	1044.0	0.158	0.375	0.250	−588
Co_3Ge $\rightleftharpoons$ hcp + Co_5Ge_3	eutectoid	922.8	0.250	0.150	0.375	−463
hcp + Co_5Ge_3 $\rightleftharpoons$ Co_5Ge_2	peritectoid	908.6	0.149	0.375	0.286	−613
fcc $\rightleftharpoons$ hcp	congruent	695.3	0.000	0.000		−428
Co_5Ge_2 $\rightleftharpoons$ hcp + Co_5Ge_3	eutectoid	655.8	0.286	0.135	0.375	−403

Table IIIa. Integral quantities for the liquid phase at 1823 K.

x_{Ge}	ΔG_m [J/mol]	ΔH_m [J/mol]	ΔS_m [J/(mol·K)]	G_m^E [J/mol]	S_m^E [J/(mol·K)]	ΔC_P [J/(mol·K)]
0.000	0	0	0.000	0	0.000	0.000
0.100	−30063	−11514	10.175	−25135	7.472	0.000
0.200	−50222	−18422	17.444	−42637	13.283	0.000
0.300	−62532	−21491	22.513	−53273	17.434	0.000
0.400	−68012	−21489	25.520	−57811	19.924	0.000
0.500	−67526	−19185	26.518	−57020	20.754	0.000
0.600	−61868	−15345	25.520	−51667	19.924	0.000
0.700	−51780	−10739	22.513	−42521	17.434	0.000
0.800	−37934	−6134	17.444	−30349	13.283	0.000
0.900	−20847	−2298	10.175	−15919	7.472	0.000
1.000	0	0	0.000	0	0.000	0.000

Reference states: Co(liquid), Ge(liquid)

Table IIIb. Partial quantities for Co in the liquid phase at 1823 K.

x_{Co}	ΔG_{Co} [J/mol]	ΔH_{Co} [J/mol]	ΔS_{Co} [J/(mol·K)]	G^E_{Co} [J/mol]	S^E_{Co} [J/(mol·K)]	a_{Co}	γ_{Co}
1.000	0	0	0.000	0	0.000	1.000	1.000
0.900	−5542	−2431	1.706	−3945	0.830	0.694	0.771
0.800	−18138	−8702	5.176	−14755	3.321	0.302	0.378
0.700	−36301	−17274	10.437	−30895	7.472	0.091	0.130
0.600	−58572	−26614	17.530	−50829	13.283	0.021	0.035
0.500	−83526	−35185	26.518	−73020	20.754	0.004	0.008
0.400	−109821	−41450	37.505	−95933	29.886	0.001	0.002
0.300	−136280	−43874	50.689	−118031	40.679	0.000	0.000
0.200	−162174	−40920	66.513	−137779	53.132	0.000	0.000
0.100	−188542	−31054	86.389	−153641	67.245	0.000	0.000
0.000	−∞	−12738	∞	−164080	83.018	0.000	0.000

Reference state: Co(liquid)

Table IIIc. Partial quantities for Ge in the liquid phase at 1823 K.

x_{Ge}	ΔG_{Ge} [J/mol]	ΔH_{Ge} [J/mol]	ΔS_{Ge} [J/(mol·K)]	G^E_{Ge} [J/mol]	S^E_{Ge} [J/(mol·K)]	a_{Ge}	γ_{Ge}
0.000	−∞	−140738	∞	−292080	83.018	0.000	0.000
0.100	−250750	−93262	86.389	−215849	67.245	0.000	0.000
0.200	−178558	−57304	66.513	−154163	53.132	0.000	0.000
0.300	−123736	−31330	50.689	−105487	40.679	0.000	0.001
0.400	−82173	−13802	37.505	−68285	29.886	0.004	0.011
0.500	−51526	−3185	26.518	−41020	20.754	0.033	0.067
0.600	−29900	2058	17.530	−22157	13.283	0.139	0.232
0.700	−15565	3462	10.437	−10159	7.472	0.358	0.512
0.800	−6873	2562	5.176	−3491	3.321	0.635	0.794
0.900	−2214	897	1.706	−617	0.830	0.864	0.960
1.000	0	0	0.000	0	0.000	1.000	1.000

Reference state: Ge(liquid)

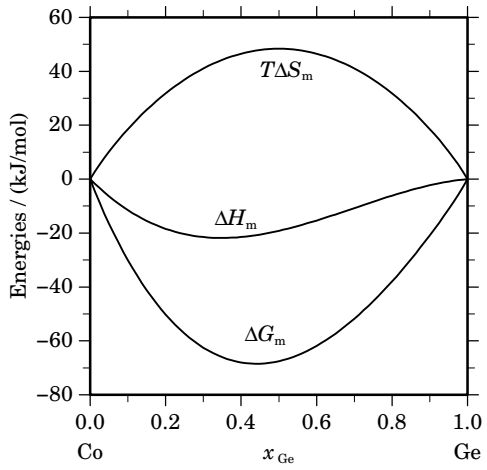

Fig. 2. Integral quantities of the liquid phase at T=1823 K.

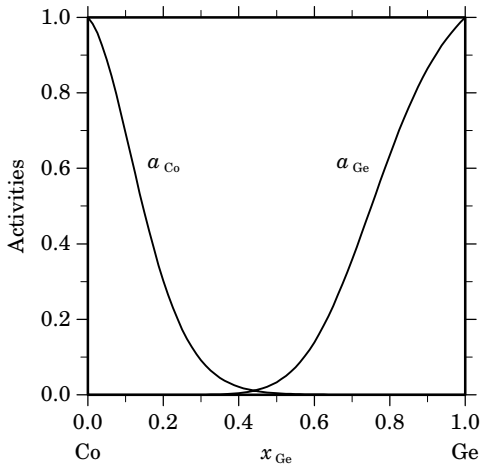

Fig. 3. Activities in the liquid phase at T=1823 K.

Table IV. Standard reaction quantities at 298.15 K for the compounds per mole of atoms.

Compound	x_{Ge}	$\Delta_{\mathrm{f}}G^{\circ}$ / (J/mol)	$\Delta_{\mathrm{f}}H^{\circ}$ / (J/mol)	$\Delta_{\mathrm{f}}S^{\circ}$ / (J/(mol·K))	$\Delta_{\mathrm{f}}C_P^{\circ}$ / (J/(mol·K))
Co_3Ge_1	0.250	−41387	−39698	5.668	−0.109
Co_5Ge_2	0.286	−47219	−46188	3.458	−0.104
Co_5Ge_3	0.375	−60000	−60000	0.001	−0.287
Co_1Ge_1	0.500	−51800	−51800	0.001	−0.228
Co_5Ge_7	0.583	−44163	−44167	−0.015	−0.060
Co_1Ge_2	0.667	−36403	−37120	−2.405	−0.149

References

[1949Pfi] H. Pfisterer, K. Schubert: Z. Metallkd. **40** (1949) 378–383.
[1952Kös] W. Köster, E. Horn: Z. Metallkd. **43** (1952) 333–33.
[1973Aga] T.P. Agalakova, V.L. Zagryzhskii, P.V. Geld: Izv. Akad. Nauk SSSR, Neorg. Mater. **9** (1973) 1180–1185; TR: Inorg. Mater. **9** (1973) 1048–1051.
[1976Bal] J.B. Ballance, H. Stadelmaier: Z. Metallkd. **67** (1976) 729–731.
[1980Day] A. Dayer, P. Feschotte: J. Less-Common Met. **72** (1980) 51–70.
[1990Eno] H. Enoki, K. Ishida, T. Nishizawa: J. Less-Common Met. **160** (1990) 153–160.
[1991Ish] K. Ishida, T. Nishizawa: J. Phase Equilibria **12** (1991) 77–83.
[2004Kor] J. Korb, unpublished assessment, GTT-Technologies, 2004.