

The Cr-Ge (Chromium-Germanium) System

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Equilibrium Diagram

The assessed equilibrium phase diagram of the Cr-Ge system is given in Fig. 1. The following stable phases are present in the system:

- The liquid, L
- The terminal solid solution, (Cr), with a maximum solubility of approximately 11 at.% Ge at the peritectic temperature of 1564 °C
- The terminal solid solution, (Ge), with a maximum solid solubility of approximately 0.3 at.% Cr at the eutectic temperature of 895 °C
- Cubic Cr_3Ge , which decomposes peritectically at 1564 °C
- Tetragonal Cr_5Ge_3 , which decomposes peritectically at 1262 °C and undergoes a polymorphic transformation at 1002 °C
- Orthorhombic $\text{Cr}_{11}\text{Ge}_8$, which decomposes peritectically at 1170 °C
- Cubic CrGe , which decomposes peritectically at 998 °C
- Tetragonal $\text{Cr}_{11}\text{Ge}_{19}$, which decomposes peritectically at 928 °C

Composition and temperature data of monovariant and invariant phase equilibria are given in Table 1.

Table 1 Monovariant and Invariant Equilibria in the Cr-Ge System

Reaction	Compositions of the respective phases, at.% Ge			Temperature, °C	Reaction type
$(\text{Cr}) + \text{L} \rightleftharpoons \text{Cr}_3\text{Ge}$.11	29	22.8	1564	Peritectic
$\text{Cr}_3\text{Ge} + \text{L} \rightleftharpoons \text{Cr}_5\text{Ge}_3$.25.1	47	37.8	1262	Peritectic
$\text{Cr}_5\text{Ge}_3 + \text{L} \rightleftharpoons \text{Cr}_{11}\text{Ge}_8$.38.2	53	42.1	1170	Peritectic
$\text{Cr}_{11}\text{Ge}_8 + \text{L} \rightleftharpoons \text{CrGe}$.42.1	68	50	998	Peritectic
$\text{CrGe} + \text{L} \rightleftharpoons \text{Cr}_{11}\text{Ge}_{19}$.50	78	63.34	928	Peritectic
$\text{L} \rightleftharpoons \text{Cr}_{11}\text{Ge}_{19} + (\text{Ge})$.85	63.34	99.7	895	Eutectic
$\text{L} \rightleftharpoons (\text{Cr})$ (a)		0		1863 ± 20	Melting
$\text{L} \rightleftharpoons (\text{Ge})$ (a)		100		938.3	Melting

(a) From [Melt].

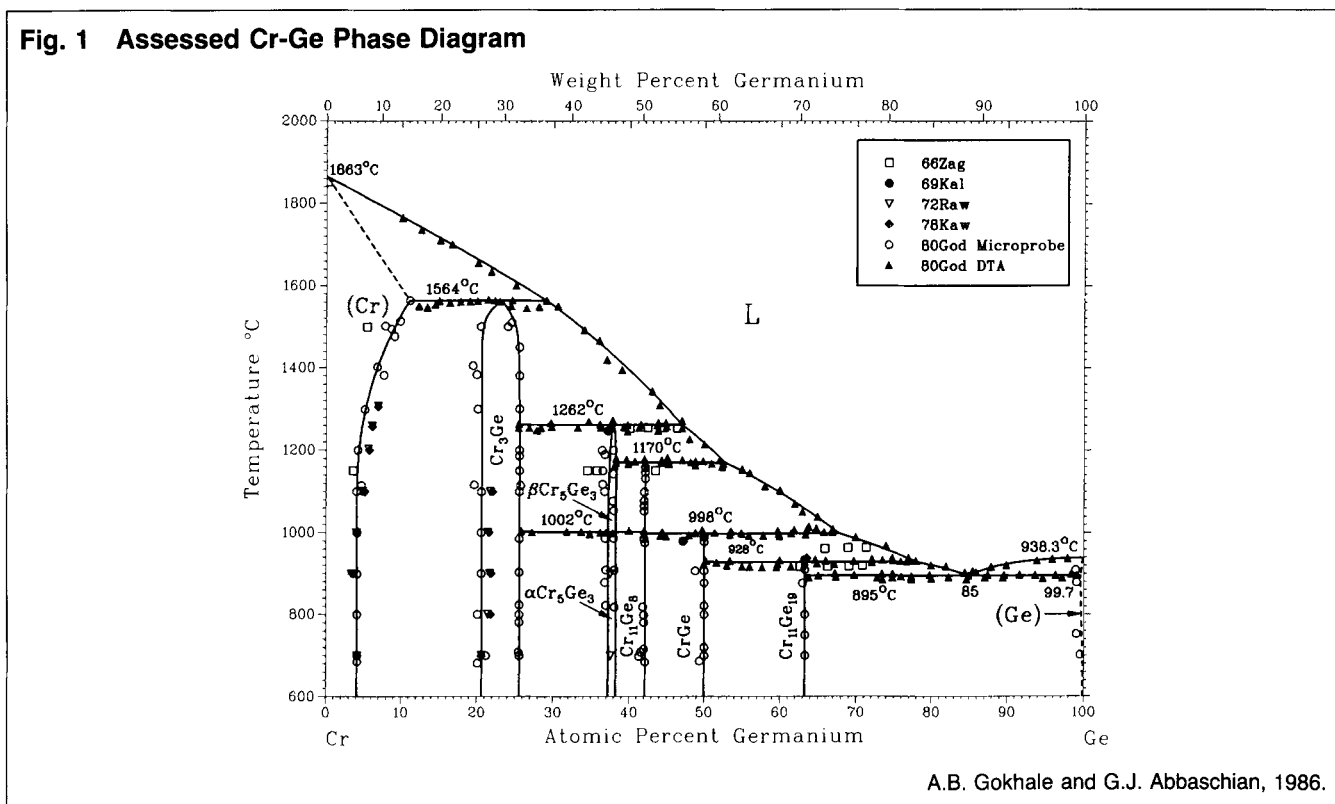


Table 2 Cr-Ge Experimental Liquidus Data

Temperature, °C	Composition, at.% Ge	Temperature, °C	Composition, at.% Ge
1492.....	34	1038.....	65
1466.....	36	1008.....	67
1420.....	37	989.....	70
1395.....	39	968.....	74
1343.....	43	938.....	77
1309.....	44	931.....	78
1271.....	47	920.....	80
1253.....	47	917.....	82
1226.....	48	903.....	86
1213.....	50	916.....	88
1175.....	52	920.....	90
1153.....	55	923.....	92
1144.....	56	931.....	94
1112.....	58	931.....	96
1102.....	60	935.....	96
1069.....	62	934.....	97
1050.....	63	936.....	98

From [80God].

A complete determination of the Cr-Ge phase diagram was carried out by [80God]. The purity of materials was 4N Cr and 4N Ge. [80God] synthesized their alloys in alumina crucibles in an argon atmosphere, followed by thermal treatments in sealed silica tubes. [80God] used X-ray diffraction, electron microprobe, microhardness, optical microscopy, and differential thermal analysis in their phase diagram determination. In addition, they used "Tammann stages" (*i.e.*, the amount of microconstituents) for determining the end compositions of the invariant reactions. The melting losses in the alloys were determined by using spectrophotometric plasma emission analysis.

[66Zag] also carried out a complete determination of the Cr-Ge phase diagram. The purity of materials was 99.98% Cr and 4N Ge. The Cr-rich alloys were synthesized in alumina crucibles under an argon atmosphere, and the Ge-rich alloys were prepared in sealed quartz tubes. [66Zag] used optical microscopy, X-ray diffraction, and differential thermal analysis for determining the phase equilibria, but apparently they did not take into account any melting losses.

[72Raw] carried out a limited study of the Cr-rich side of the diagram in the temperature range 700 to 1300 °C. The purity of materials used was 99.95% Cr and 3N Ge. Alloys containing up to 27 at.% Ge were arc melted in water-cooled copper crucibles, whereas alloys containing more Ge were induction melted in pure alumina crucibles. Both types were prepared under an argon atmosphere. The alloys were subsequently annealed in sealed, fused silica tubes and examined by X-ray diffraction and metallography. [72Raw] did not determine the liquidus or three-phase equilibria in the system, but they conducted a structural analysis of the Cr-rich intermediate phases. The crystal structure (by X-ray diffraction) and magnetic and thermoelectric properties of CrGe and Cr₁₁Ge₁₉ were studied by [78Kaw]. The purity of their materials was 5N Ge and 5N Cr.

According to our assessment, the data of [80God] are the most reliable to date, on the basis of the experimental techniques utilized and the large amount of data generated. A comparison of the data of [80God] and [66Zag]

shows that there are a number of significant differences between the two. One difference is in the invariant reaction temperatures. Those given by [66Zag] are consistently higher than those of [80God] in the Ge-rich side of the diagram. The differences may be due to the fact that [66Zag] used a Ge melting temperature that was approximately 25 °C higher than the currently accepted value. When the standard melting point of Ge is used as a correction factor, the invariant reaction temperatures of [66Zag] are close to those determined by [80God]. Another difference in the data of [66Zag] and [80God] is in the liquid-solid compositions of the invariant reactions. Also, [66Zag] reported that Cr₃Ge forms congruently from the liquid, in contrast to [80God], who showed it to form peritectically. These differences may be due to the rather speculative nature of the liquidus given by [66Zag].

The data of [72Raw] at low temperatures agree fairly well with those of [80God], particularly the solubility limit of Ge in (Cr) and the range of homogeneity of Cr₃Ge. [72Raw] indicated that Cr₃Ge, Cr₅Ge₃, and Cr₁₁Ge₈ (incorrectly reported as Cr₄Ge₃) form congruently from the liquid, in contrast to [80God], who indicated that they form as a result of peritectic reactions. The discrepancy may again be due to the speculative nature of the liquidus and insufficient data in the study by [72Raw]. [78Kaw] reported decomposition temperatures of 998 and 935 °C for CrGe and Cr₁₁Ge₁₉, respectively. The decomposition temperature for CrGe is identical to that reported by [80God], and that for Cr₁₁Ge₁₉ is very close to 928 °C, as reported by [80God].

[69Kal] mentioned that Cr₅Ge₃, CrGe, and Cr₁₁Ge₁₉ form peritectically, in agreement with the findings of [80God]. The reported peritectic reaction temperatures were 1245, 995, and 925 °C, respectively, which agree quite well with those of [80God]. The purity of materials used by [69Kal] was 99.98% Cr and 99.98% Ge. [69Kal] utilized metallographic and X-ray diffraction methods for phase analysis and adiabatic calorimetry for heat capacity measurements of the intermediate phases in the temperature range 60 to 300 K.

Liquid Solution. Experimental liquidus points transcribed from the graphical data of [80God] are given in Table 2. The liquidus was reported to be accurate to ±10 °C at compositions lower than 30 at.% Ge and to ±5 °C at compositions greater than 30 at.% Ge. However, those limits may be somewhat doubtful because the melting temperature of pure Cr has been determined with an accuracy of only ±20 °C.

Solid Solutions, (Ge) and (Cr). The maximum solid solubility of Ge in (Cr) is approximately 11 at.% at the peritectic temperature of 1564 °C, as reported by [80God]. In contrast, [72Raw] reported a value of 8 to 9 at.% Ge, and [66Zag] indicated a much lower value of approximately 5 at.% Ge as the maximum solubility. Because the values reported by [72Raw] and [66Zag] were obtained by extrapolation, the data of [80God] are preferred in this evaluation. The solubility data of various investigations show fairly good agreement at lower temperatures, as shown in Fig. 1. The solubility decreases to about 4 at.% Ge at 700 °C.

Cr₃Ge. This intermediate phase is the richest in Cr. The phase equilibrium data of several investigators for Cr₃Ge

Table 3 Data on Cr-Ge Intermediate Phases

Phase	Formation temperature, °C	Reaction type	Homogeneity range, at.% Ge	Comment	Reference
Cr ₃ Ge	1527	Congruent	21.82 to 26.36	(a)	[66Zag]
	1500	Congruent	21.78 to 24.7	(b)	[72Raw]
	1564	Peritectic	20.5 to 25.1	(c)	[80God]
Cr ₅ Ge ₃	1250	Peritectic	35.45 to 37.27	(d)	[66Zag]
	1395	Congruent	Nil	...	[72Raw]
	1262	Peritectic	37.41 to 38.2	(e)	[80God]
	1245	Peritectic	...	(e)	[69Kal]
Cr ₁₁ Ge ₈	1160	Peritectic	Nil	...	[66Zag]
	1170	Peritectic	Nil	(f)	[80God]
	1250	Congruent	Nil	(g)	[72Raw]
CrGe	1025	Peritectic	Nil	(h)	[66Zag]
	998	Peritectic	Nil	(f)	[80God]
	995	Peritectic	Nil	...	[69Kal]
	998	(j)	[78Kaw]
Cr ₁₁ Ge ₁₉	955	Peritectic	Nil	(a)	[66Zag]
	925	Peritectic	...	(b)	[69Kal]
	935	[78Kaw]
	928	Peritectic	Nil	(c)	[80God]

(a) At 1250 °C; decreased to about 1.8 at.% Ge at 800 °C. (b) At 700 °C; range stable at lower temperatures. (c) Preferred; range stable at lower temperatures. (d) Range stable at lower temperatures. (e) Homogeneity range not mentioned. (f) Preferred. (g) Incorrectly ascribed the formula Cr₄Ge₃ to the compound. (h) Also reported the melting point of Ge to be approximately 25 °C higher than the standard. (j) Did not report reaction type or homogeneity range.

are summarized in Table 3. As mentioned above, the data of [66Zag] and [72Raw] are somewhat speculative at temperatures near the liquidus. On the other hand, [80God] investigated the liquidus more thoroughly, using several experimental techniques. Consequently, the findings of [80God] are preferred in this evaluation.

Several investigators [66Zag, 72Raw, 80God, 80Kol] determined the crystal structure of Cr₃Ge to be cubic. [80Kol] studied the magnetic susceptibility of the phase (see "Magnetism," below). [75Sur] measured the heat capacity of Cr₃Ge as a function of temperature, and [80God] determined the latent heat of fusion (see "Thermodynamics," below).

Cr₅Ge₃. The data of three investigators [66Zag, 72Raw, 80God] for this phase are summarized in Table 3. The data of [80God] are preferred for the reasons mentioned above. The data of [69Kal] are also included in Table 3. [69Kal] did not mention either the experimental technique used or the range of homogeneity of the phase. [58Par], [72Raw], [66Zag], and [80Kol] determined the crystal structure of the phase to be tetragonal. [80Kol] studied the magnetic susceptibility of Cr₅Ge₃ (see "Magnetism," below). [75Sur] measured the heat capacity of Cr₅Ge₃ as a function of temperature, and [80God] determined its latent heat of fusion (see "Thermodynamics," below). [80God] reported an allotropic transformation of this phase as 1002 °C and measured the latent heat of transformation. The crystal structure of the high-temperature form is unknown.

Cr₁₁Ge₈. [66Zag] reported this phase to form peritectically at 1160 °C. This agrees fairly well with the data of [80God], who reported formation of the phase through a peritectic reaction at 1170 °C. The data of these investigators show no range of homogeneity for the phase. [72Raw] incorrectly identified Cr₁₁Ge₈ as Cr₄Ge₃, and they reported that the phase melts congruently. The data of various investigators are listed in Table 3. The crystal structure of this phase was determined by several inves-

tigators [66Zag, 74Isr, 72Raw, 80God] to be orthorhombic. [80God] also determined the latent heat of fusion of the phase (see "Thermodynamics," below).

CrGe. Several investigators reported that this phase forms peritectically [66Zag, 80God, 69Kal]. [78Kaw] reported the formation temperature of the phase as 925 °C, but did not indicate the type of reaction. The temperatures reported by [80God], [69Kal], and [78Kaw] are in good agreement, whereas that reported by [66Zag] differs substantially (Table 3). For reasons mentioned above, the data of [80God] are preferred. The crystal structure of this cubic phase was determined by [66Zag], [78Kaw], [80Kol], and [80God]. The magnetic susceptibility of the phase as a function of temperature was measured by [80Kol] (see "Magnetism," below). [69Kal] measured the heat capacity of the phase as a function of temperature, and [80God] measured its latent heat of fusion (see "Thermodynamics," below).

Cr₁₁Ge₁₉. [66Zag], [69Kal], and [80God] determined that this phase forms peritectically (Table 3). [78Kaw] also measured the formation temperature of the phase, but did not mention the type of reaction. The temperatures reported by [69Kal], [78Kaw], and [80God] show good agreement, whereas that reported by [66Zag] differs considerably. The crystal structure of the tetragonal phase was determined by several investigators [66Zag, 80God, 80Kol, 67Vol, 78Kaw]. The magnetic susceptibility of the phase was measured by [80Kol] (see "Magnetism," below). The heat capacity of the phase was measured as a function of temperature by [69Kal], and the latent heat of fusion was determined by [80God] (see "Thermodynamics," below).

Crystal Structures and Lattice Parameters

The preferred crystal structure and lattice parameter data are summarized in Tables 4 and 5. Our preference is based on the completeness of each investigation and the

Table 4 Cr-Ge Crystal Structure Data

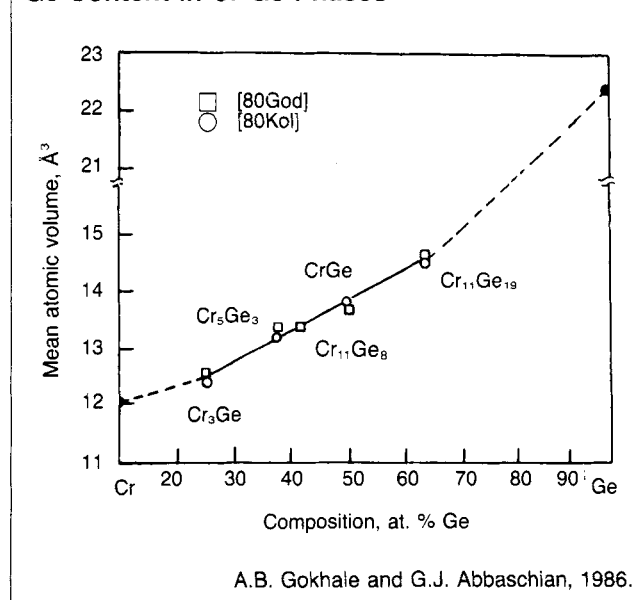
Phase	Homogeneity, at.% Ge	Pearson symbol	Space group	Strukturbericht designation	Proto-type	Reference
(Cr)	0	<i>cI2</i>	<i>Im3m</i>	A2	W	[King1]
Cr ₃ Ge	20.5 to 25.1	<i>cP8</i>	<i>Pm3n</i>	A15	Cr ₃ Si	[80Kol]
Cr ₅ Ge ₃	37.41 to 38.2	<i>tI32</i>	<i>I4/mcm</i>	D8 _m	W ₅ Si ₃	[80Kol]
Cr ₁₁ Ge ₈	42.1	<i>oP76</i>	<i>Pnam</i>	...	Mn ₁₁ Ge ₈	[74Isr]
CrGe	50	<i>cP8</i>	<i>P2₁3</i>	B20	FeSi	[80Kol]
Cr ₁₁ Ge ₁₉ (a)	63.34	...	<i>P4n2</i>	...	Mn ₁₁ Si ₁₉	[80Kol]
(Ge)	100	<i>cF8</i>	<i>Fd3m</i>	A4	C(diamond)	[King1]

(a) Tetragonal.

Table 5 Cr-Ge Lattice Parameter Data

Phase	Composition, at.% Ge	Lattice parameters, nm			Reference
		a	b	c	
(Cr)	0	0.28847	[King1]
Cr ₃ Ge	20.5 to 25.1	0.4631(1)	[80Kol]
Cr ₅ Ge ₃	37.41 to 38.2	0.9410(7)	...	0.4783(5)	[80Kol]
Cr ₁₁ Ge ₈	42.1	1.3171	1.5775	0.4939	[74Isr]
CrGe	50	0.4796(9)	[80Kol]
Cr ₁₁ Ge ₁₉	63.34	0.579(1)	...	5.187(30)	[80Kol]
(Ge)	100	0.56574	[King1]

Fig. 2 Mean Atomic Volume as a Function of Ge Content in Cr-Ge Phases



range of experimental techniques utilized. No major differences in the studies of various investigators were found. The lattice parameters generally were found to vary in the third digit, and the space groups, when assigned, were in agreement.

The mean atomic volumes of the intermediate phases were measured by [80God] and [80Kol]. Their results show excellent agreement and are plotted in Fig. 2 along with the atomic volumes of the components. The mean atomic volume increases with increasing Ge content. According to [80God] and [80Kol], this could be interpreted as an increase in the Cr-Cr distance with increasing Ge concentration.

Table 6 Enthalpy of Mixing of Cr-Ge Alloys

Composition, at. fraction Ge	Enthalpy of mixing ($-\Delta_{\text{mix}}H$), kJ/mol	Composition, at. fraction Ge	Enthalpy of mixing ($-\Delta_{\text{mix}}H$), kJ/mol
0.936	1.171	0.624	8.033
0.87	1.924	0.598	10.125
0.844	2.928	0.559	10.25
0.768	3.932	0.554	11.798
0.735	6.151	0.498	12.844
0.679	6.652	0.462	14.184
0.664	7.865	0.42	15.481

From [79Shl].

Thermodynamics

The enthalpies of mixing of Cr-Ge alloys at 1773 K and in the range 42 to 93.6 at.% Ge were measured calorimetrically by [79Shl] (see Table 6). In the present evaluation, a third degree polynomial was fitted to the data of [79Shl]; the resulting equation representing the integral molar enthalpy of mixing as a function of composition is as follows:

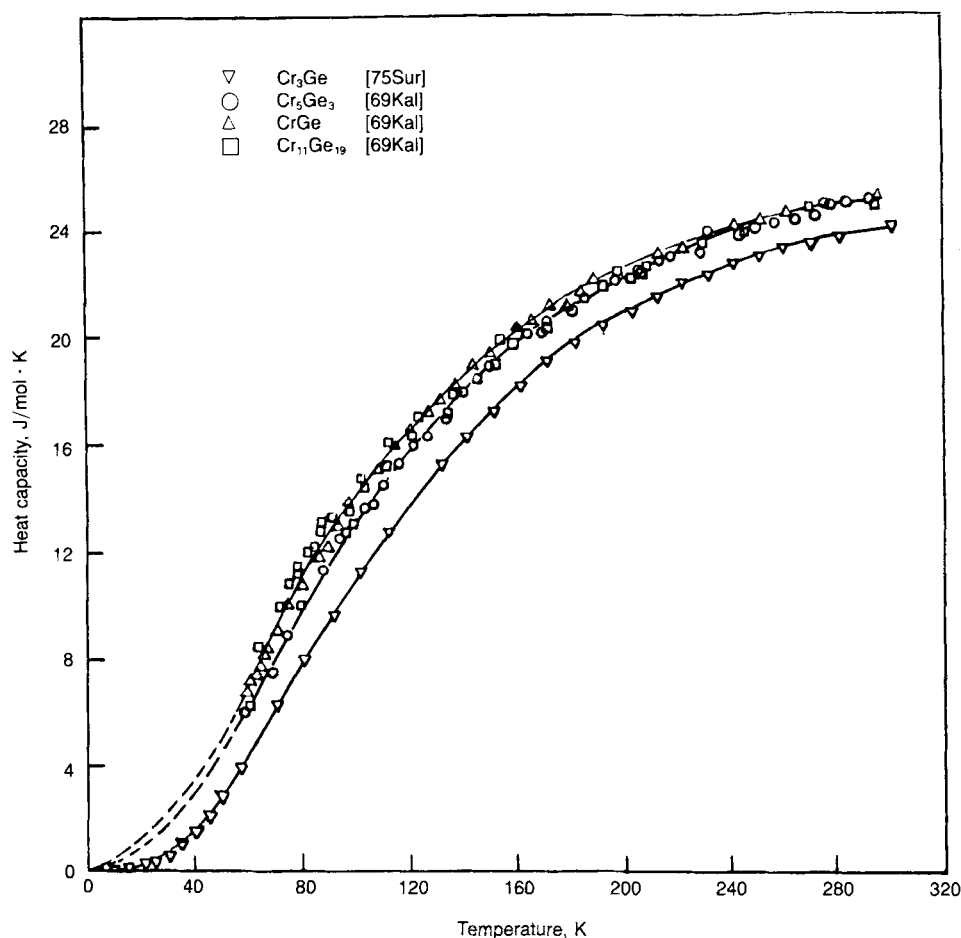
$$\Delta_{\text{mix}}H = X_{\text{Ge}}(1 - X_{\text{Ge}})(-148.97 + 256.02 X_{\text{Ge}} - 123.43 X_{\text{Ge}}^2) \text{ kJ/mol}$$

where X_{Ge} is the atom fraction of Ge.

The enthalpies of mixing calculated on the basis of this equation showed excellent agreement with the data of [79Shl]. The equation indicates the enthalpy of mixing in the liquid to be: (a) exothermic, (b) nonsymmetric with respect to composition, and (c) with a maximum of 17.5 kJ/mol at 30 at.% Ge.

The excess entropy of mixing was assessed by using this enthalpy of mixing expression and the experimental solubility data of [80God]. The excess entropy of mixing was represented by a third degree polynomial as follows:

Fig. 3 Heat Capacity of Cr-Ge Phases as a Function of Temperature



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Table 7 Experimental and Calculated Formation Temperatures of Cr-Ge Alloys

Phase	Formation temperature, °C	
	experimental	calculated
Cr ₃ Ge	1564	1565
Cr ₅ Ge ₃	1262	1324
Cr ₁₁ Ge ₈	1170	1229
CrGe	998	1094
Cr ₁₁ Ge ₁₉	928	941

Note: Experimental temperatures determined by [80God]; calculated temperatures from present thermodynamic modeling.

$$S^{\text{ex}} = X_{\text{Ge}} (1 - X_{\text{Ge}}) (-95.48 + 147.88 X_{\text{Ge}} - 70.06 X_{\text{Ge}}^2) \text{ J/mol} \cdot \text{K}$$

where X_{Ge} is the atom fraction of Ge.

The equation indicates the mixing process to be nonrandom. The excess Gibbs energy of mixing appears to be positive over the entire temperature and composition range of liquid stability, indicating a positive departure from Raoultian behavior. It should be noted that the en-

thalpy and excess entropy of mixing have been assumed to be temperature independent.

A phase diagram was calculated on the basis of these expressions for the enthalpy and excess entropy of mixing, and the Gibbs energies of fusion for the pure components. The calculated diagram showed a fair agreement with the experimentally determined diagram. In particular, the calculations correctly predicted the formation of the intermediate phases through peritectic reactions, as well as the presence of a eutectic between Cr₁₁Ge₁₉ and (Ge). The predicted and experimental formation temperatures for the intermediate phases are listed in Table 7.

The Gibbs energies of fusion for the pure components were calculated as follows:

$$\Delta_{\text{fus}}G_{\text{Cr}} = 7598.68 + 143.52 T + 7.7655 \times 10^{-3} T^2 - 21.32 T \ln T - 8.35 \times 10^5 T^{-1} \text{ J/mol}$$

$$\Delta_{\text{fus}}G_{\text{Ge}} = 32938.8 + 23.43 T + 3.678 \times 10^{-3} T^2 - 7.761 T \ln T \text{ J/mol}$$

where T is in K.

Table 8 Thermodynamic Properties of Chromium Germanides

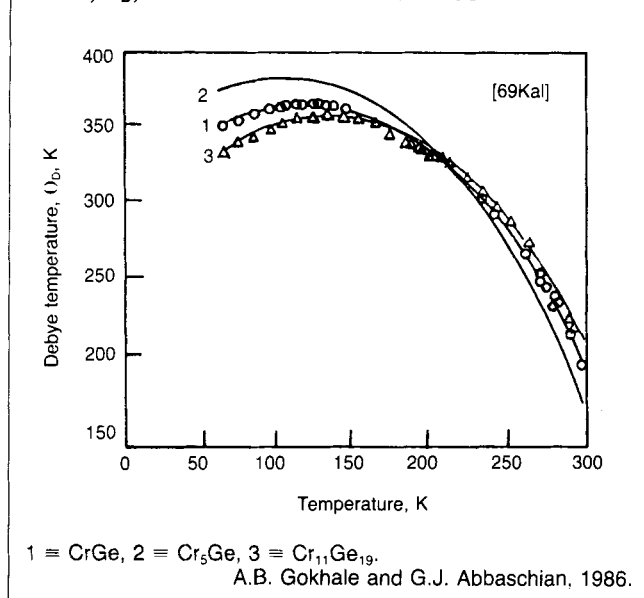
Phase	Heat capacity ($C_p(298)$), J mol ⁻¹ · K	Enthalpy of formation ($\Delta_f H^\circ(298)$), J · mol	Entropy of formation ($\Delta_f S(298)$), J/mol · K	Latent heat of transformation(a), kJ · mol	Reference
Cr ₅ Ge	24.07	4325	26.0	15.48 ± 2.5	[75Sur]
Cr ₅ Ge ₃	25.16	4720	29.6	8.37 ± 1.3	[69Kal]
Cr ₁₁ Ge ₅	8.37 ± 1.3	
CrGe	25.16	4810	30.6	8.79 ± 1.3	[69Kal]
Cr ₁₁ Ge ₁₉	25.16	4880	31.7	10.46 ± 1.3	[69Kal]
Cr ₅ Ge ₃	1.26(b)	

Note: The entity for a mole is an atom.
(a) The latent heat data are from [80God]. (b) Allotropic transformation.

Table 9 Magnetic Susceptibility of Cr-Ge Phases

Phase	Temperature range, K	Method	Result	Atomic susceptibility, $\chi_g \times 10^6$ emu/Cr atom · O _e	Molecular susceptibility, $\chi_M \times 10^6$ emu/g · mol · O _e	Comment
(Cr)	RT	3.6	187.23	...
Cr ₅ Ge	100 to RT	Sucksmith balance	Pauli paramagnetic	1.94	150.75	(a)
Cr ₅ Ge ₃	100 to RT	Sucksmith balance	Pauli paramagnetic	2.9	282.33	(a)
CrGe	4.2 to 300	Faraday balance	Paramagnetic	6.78	853.56	(b)
	300 to 800	Modified Sucksmith balance				
Cr ₁₁ Ge ₁₉	4.2 to 420	Magnetometry	Ferromagnetic	24.17	4303.05	(c)
(Ge)	RT	-0.12

Note: RT = room temperature. From [80Kol]. (a) Susceptibility is independent of temperature. (b) Obeys the Curie-Weiss law above 150 K and deviates from the Curie-Weiss law below 150 K. The deviation may be ascribed to small amounts of residual Cr₁₁Ge₁₉. (c) Curie temperature, $T_C = 91$ K.

Fig. 4 Variation of Characteristic Temperatures, θ_D , of Chromium Germanides

The heats of fusion and heat capacities for the pure components used in the calculation are from [77Bar].

The heats of the peritectic transformations were determined by [80God] using differential thermal analysis, and are listed in Table 8. The heat capacity of Cr₅Ge was measured by [75Sur] in the temperature range 5 to 300 K using adiabatic calorimetry. The heat capacities of

Cr₅Ge₃, CrGe, and Cr₁₁Ge₁₉ were measured similarly by [69Kal] in the temperature range 50 to 300 K. [69Kac] further calculated the characteristic Debye temperatures for the three germanides as a function of temperature. The heat capacity data are plotted in Fig. 3. The plot of Debye temperature as a function of temperature is shown in Fig. 4.

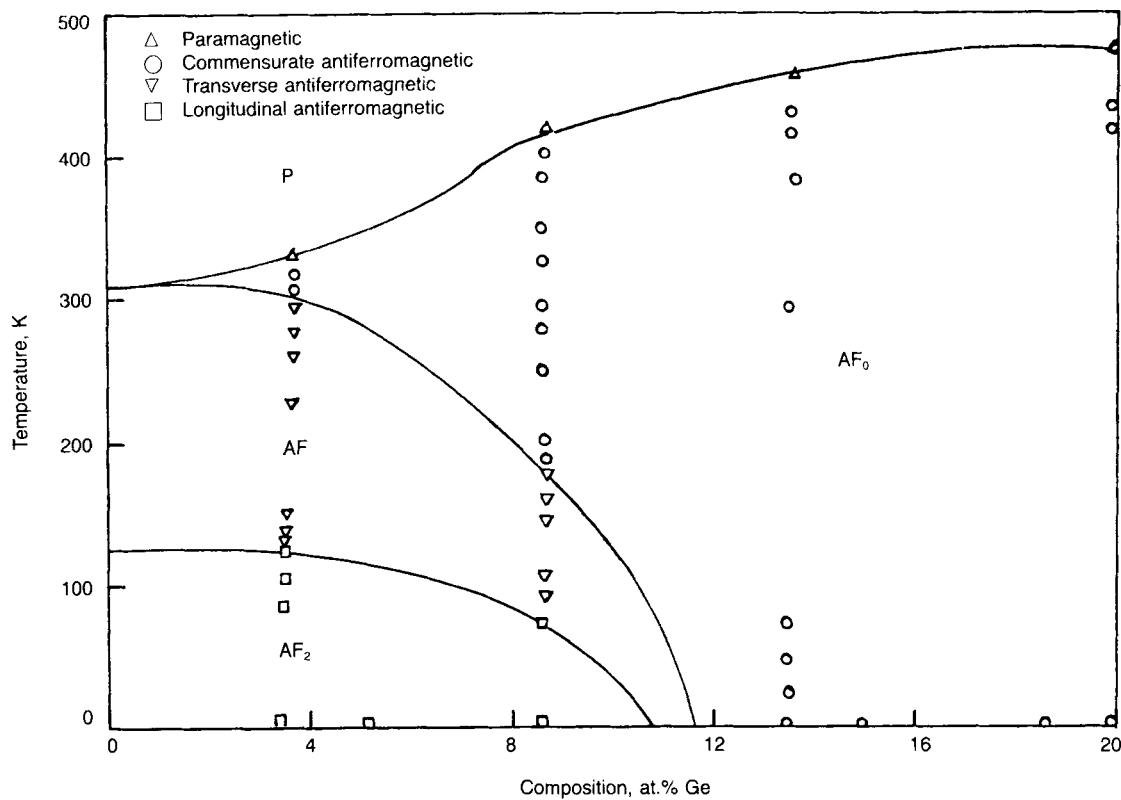
The standard entropies and enthalpies of formation for the intermediate phases, calculated by extrapolating the measured heat-capacity data to absolute zero, are listed in Table 8.

Magnetism

A partial magnetic study of the Cr-Ge system was reported by [83Boo] (Fig. 5). Using neutron diffraction measurements, they studied the stability of paramagnetic and antiferromagnetic states as a function of temperature for alloys in the range 0 to 20 at.% Ge. The boundaries delineating the different regions in Fig. 5 are only approximate, due to insufficient data. [83Boo] showed that in this system, the commensurate phase (indicated as AF0 in Fig. 5) is stabilized above 0 K by the addition of approximately 1 at.% Ge.

[80Kol] carried out a detailed magnetic and structural study of the intermediate phases in the Cr-Ge system. The purity of materials was 5N Cr and 5N Ge. They used X-ray photoelectron spectroscopy, X-ray and neutron diffraction, electron spectroscopy for chemical analysis, and magnetometry. Their results on magnetic susceptibility are summarized in Table 9, and the data are plotted in Fig. 6. They indicated that Cr₅Ge₃ and Cr₅Ge are Pauli paramagnetic, whereas CrGe and Cr₁₁Ge₁₉ obey the Curie-Weiss law above 200 and 280 K, respectively. The

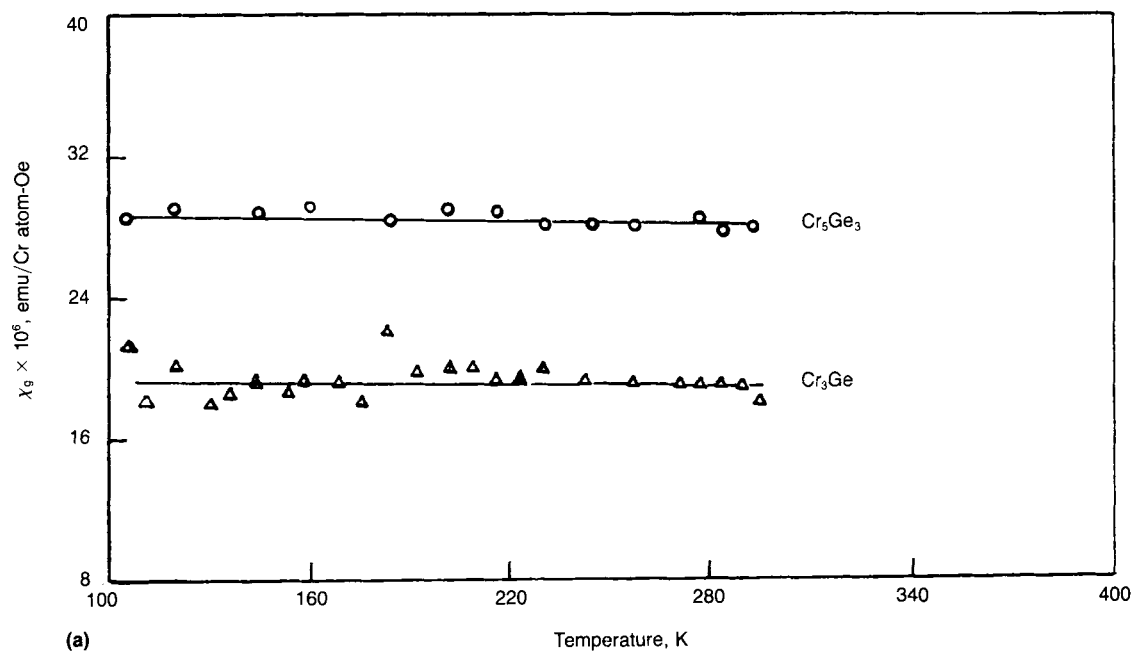
Fig. 5 Magnetic Phase Diagram of Cr-Ge System



From [83Boo].

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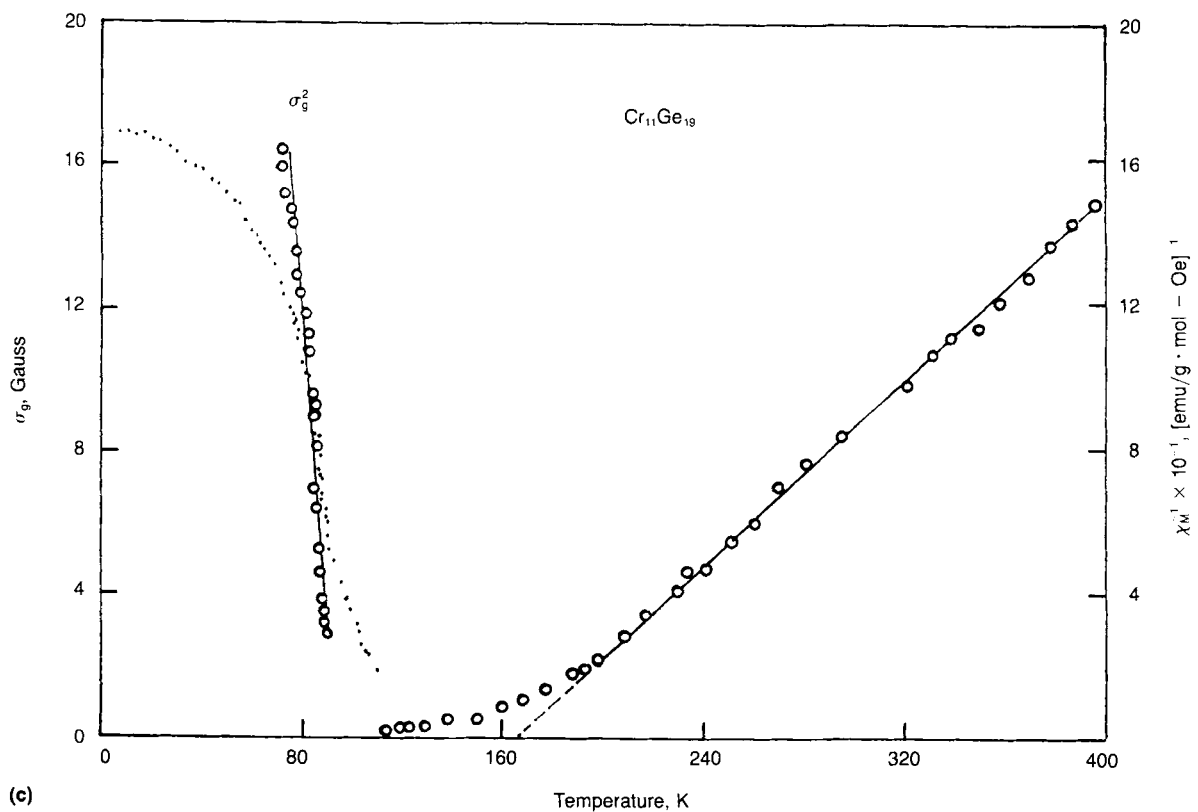
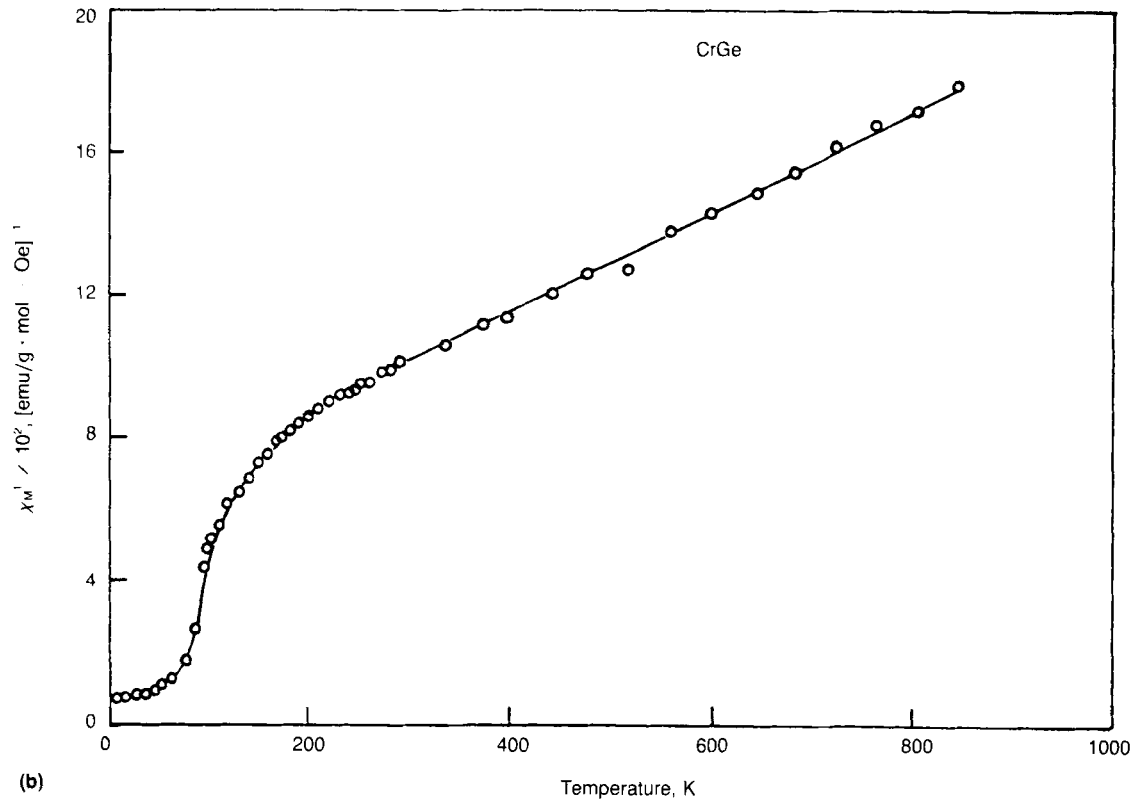
Fig. 6 Temperature Dependence of Magnetic Susceptibility of CrGe Phases

(a) Cr₅Ge and Cr₃Ge. (b) CrGe. (c) Cr₁₁Ge₁₉.

(Continued...)

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Fig. 6 Temperature Dependence of Magnetic Susceptibility of CrGe Phases (Continued)



(a) Cr₅Ge and Cr₃Ge. (b) CrGe. (c) Cr₁₁Ge₁₉.

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latter finding is supported by the studies of [78Kaw] on the magnetic susceptibility of $\text{Cr}_{11}\text{Ge}_{19}$, which indicate that the intermediate phase obeys the Curie-Weiss law above 250 K.

Cited References

- 58Par:** E. Parthé and J.T. Norton, "Crystal Structures of Zr_5Ge_3 , Ta_5Ge_3 , and Cr_5Ge_3 ," *Acta Crystallogr.*, **11**, 14-17 (1958). (Crys Structure; Experimental)
- 66Zag:** V.I. Zagryazhskii, A.K. Shtol'ts, P.V. Gel'd, and N.V. Kuz'menko, "Phase Diagram of the System Chromium-Germanium," *Sov. Powder Metall. Met. Ceram.*, **8**(44), 639-642 (1966). (Equi Diagram; Experimental)
- 67Vol:** H. Vollenkle, A. Preisinger, H. Nowotny, and A. Wittmann, "The Crystal Structures of $\text{Cr}_{11}\text{Ge}_{19}$, $\text{Mo}_{13}\text{Ge}_{23}$, and $\text{V}_{17}\text{Ge}_{31}$," *Z. Krist.*, **124**(1-2), 9-25 (1967). (Crys Structure; Experimental)
- 69Kal:** G.I. Kalishevich, V.L. Zagryazhskii, L.V. Shchivanova, N.N. Serebrennikov, and P.V. Gel'd, "Heat Capacities of Chromium Germanides at Low Temperatures," *Russ. J. Phys. Chem.*, **43**(1), 132-133 (1969). (Thermo; Experimental)
- 72Raw:** B. Rawal and K.P. Gupta, "Phase Equilibria in the Chromium-Germanium System at the High Chromium End," *J. Less-Common Met.*, **27**, 65-72 (1972). (Equi Diagram, Crys Structure; Experimental; #)
- 74Isr:** P. Israiloff, H. Völlenkle, and A. Wittmann, "Crystal Structure of the Compounds Vanadium-Germanium (V_{11}Ge_8), Chromium-Germanium ($\text{Cr}_{11}\text{Ge}_8$), and Manganese-Germanium ($\text{Mn}_{11}\text{Ge}_8$)," *Monatsh. Chem.*, **105**(6), 1387-1404 (1974). (Crys Structure; Experimental)
- 75Sur:** V.I. Surikov, G.I. Kalishevich, and P.V. Gel'd, "Thermodynamic Characteristics of Trichromium Silicide, Trichromium Germanide, Trivanadium Silicide, and Trivanadium Germanide," *Russ. J. Phys. Chem.*, **49** (2), 326-327 (1975). (Thermo; Experimental)
- 77Bar:** I. Barin, O. Knacke, and O. Kubaschewski, *Thermochemical Properties of Inorganic Substances* (Supplement), Springer-Verlag, New York (1977). (Thermo; Compilation)
- 78Kaw:** I. Kawasumi, S. Konishi, M. Kubota, and M. Sakata, "Phase Analysis and some Physical Properties of the Higher Chromium Germanides," *Jpn. J. Appl. Phys.*, **17**(12), 2173-2174 (1978). (Equi Diagram, Magnetism; Experimental)
- *79Shl:** A.N. Shlapak, E.A. Beloborodova, I.V. Nikolaenko, and G.I. Batalin, "Heat of Mixing of Liquid Solutions of Germanium with Chromium," *Ukr. Khim. Zh.*, **45**(7), 670-672 (1979). (Thermo; Experimental)
- *80God:** D. Godat and P. Feschotte, "Phase Diagram of the Chromium-Germanium System," *J. Less-Common Met.*, **72**(1), 7-22 (1980). (Equi Diagram, Thermo, Crys Structure; Experimental; #)
- 80Kol:** M. Kolenda, J. Stoch, and A. Szytula, "ESCA and Magnetic Studies of the Cr-Ge System," *J. Magn. Magn. Mater.*, **20**, 99-106 (1980). (Magnetism, Crys Structure, Thermo; Experimental)
- 83Boo:** J.G. Booth, M.M.R. Costa, and K.R.A. Ziebeck, "Magnetic Phase Diagrams for the Cr-Ga and Cr-Ge Systems," *J. Magn. Magn. Mater.*, **31-34**, 285-286 (1983). (Magnetism; Experimental)

*Indicates key paper.

#Indicates presence of a phase diagram.

Cr-Ge evaluation contributed by **A.B. Gokhale** and **G.J. Abbaschian**, Department of Materials Science and Engineering, University of Florida, Gainesville, FL 32611. This program was supported by ASM, under Grant No. FG 101-1 to the University of Florida. Thermodynamic calculations were made using the computer program at the McGill University, Montréal, Québec, developed by Drs. A.D. Pelton, W.T. Thompson, and C.W. Bale. Literature searched through 1984. Professor Abbaschian is the ASM/NBS Data Program Category Editor for binary germanium alloys.

The Si-Y (Silicon-Yttrium) System

28.0855

88.9059

By **A.B. Gokhale** and **G.J. Abbaschian**
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Equilibrium Diagram

The assessed Y-Si equilibrium diagram (Fig. 1) is based on the work of [61Lun], who determined the phase equilibria by X-ray and metallographic methods. The purity of the starting materials was not specified. According to [61Lun], the system is characterized by: three eutectic reactions, which occur at 13, 41, and 82 at.% Si and 1260, 1710, and 1215 °C, respectively; and four intermediate phases, Y_3Si_3 , Y_5Si_4 , YSi , and Y_3Si_5 . Y_5Si_3 and Y_5Si_4 melt congruently at 1850 and 1840 °C, respectively, and YSi and Y_3Si_5 form through peritectic reactions at 1835 and 1655 °C, respectively.

In addition, [61Lun] mentioned that the αY to βY transformation in the presence of Si involves a "peritectic-type" reaction. It is likely that the transformation is a metatectic (inverse peritectic) reaction, as in the Ge-Y system [72Sch]. However, the solid solubility of Si in (Y) is very small, as discussed below. Thus, in the absence of

direct experimental confirmation, the reaction has been omitted from this evaluation.

The equilibrium diagram proposed by [61Lun] has been modified by these evaluators as follows:

The liquidus is indicated as being uncertain in Fig. 1, because the X-ray and metallographic techniques utilized by [61Lun] would not yield accurate liquidus data. An allotropic transformation for Y_3Si_5 is shown at 450 °C [59Per1]. (In his review, [61Gsc] modified the system in a similar manner.)

In addition, αYSi_2 and βYSi_2 are included. βYSi_2 forms peritectically at 1520 °C [60Bin] and undergoes an allotropic transformation to αYSi_2 at 1250 °C [72May]. There is some controversy about the existence of these phases.

[61Gsc] indicated that the lattice constants for αYSi_2 determined by [59Per1] and Grinthal (quoted by [61Gsc]), are practically the same as those determined by [61Lun]