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* Indicates key paper.

\# Indicates the presence of a phase diagram.

Ge-Pr evaluation contributed by **A.B. Gokhale, A. Munitz,** and **G.J. Abbaschian,** Department of Materials Science and Engineering, University of Florida, Gainesville, FL 32611. This work was supported by ASM INTERNATIONAL under grant No. FG101-1. Thermodynamic calculations were made using the F*A*C*T* computer program at the McGill University, Montreal, Quebec, Canada. The evaluators wish to thank Dr. K.A. Gschneidner, Jr., Director, Rare Earth Information Center, Iowa State University, for his help in providing some of the literature sources. Literature searched through 1984. Professor Abbaschian is the ASM/NIST Data Program Category Editor for binary germanium alloys.

The Nd-Si (Neodymium-Silicon) System

By A.B. Gokhale, A. Munitz, and G.J. Abbaschian
University of Florida

Equilibrium Diagram

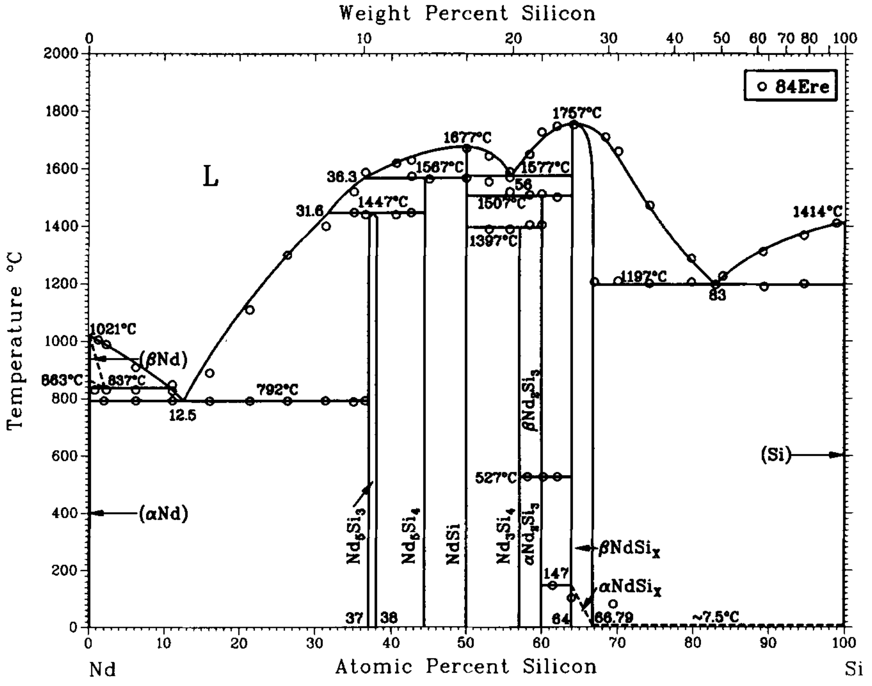
The assessed Nd-Si equilibrium diagram is shown in Fig. 1, and the monovariant and invariant equilibria are summarized in Table 1.

A complete investigation of the phase equilibria in the Nd-Si system was carried out by [84Ere], employing metallographic, X-ray diffraction and differential thermal analysis measurements. The assessed equilibrium diagram is based primarily on the work of [84Ere], with modifications incorporated on the basis of other studies on the synthesis and physical properties of various intermediate phases.

The important characteristics of the system can be summarized as follows:

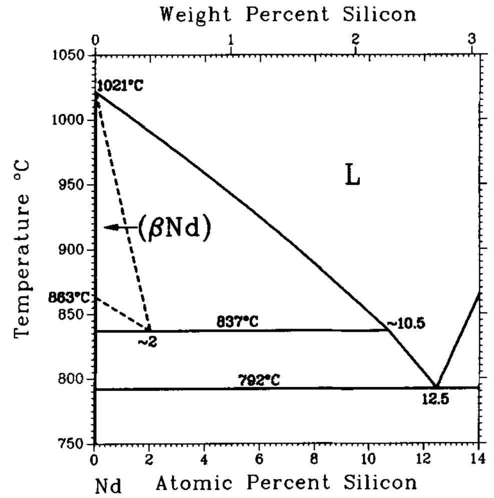
- Tetragonal Nd_5Si_3 is the richest in Nd in the system, forming peritectically at 1447 °C. [84Ere] indicated the phase to be nearly stoichiometric. However, based on the lattice parameter data of [68Ram], a homogeneity range of 1 at.% Si is indicated tentatively in this evaluation.
- Nearly stoichiometric, tetragonal Nd_5Si_4 forms peritectically at 1567 °C.
- Nearly stoichiometric, orthorhombic NdSi melts congruently at 1677 °C.
- Nearly stoichiometric, Nd_3Si_4 forms peritectoidally at 1397 °C; the structure has not been determined.
- Nearly stoichiometric, Nd_2Si_3 (reported as $NdSi_{1.5}$ by [84Ere]) forms peritectoidally at 1507 °C and undergoes an allotropic transformation at 527 °C. The low-temperature modification is hexagonal, whereas the high-temperature structure remains undetermined.
- $NdSi_x$ (reported as $NdSi_{1.8}$ by [84Ere]) melts congruently at 1757 °C. [84Ere] indicated a homogeneity range of 64 to 65 at.% Si for the phase. However, based on the synthesis data of [65Dvo1], [65Dvo2], [65Sam], and [66Dvo], the range has been extended to 66.79 at.% Si in this evaluation. [84Ere] indicated an allotropic transformation at 147 °C on the Si-deficient side (64 at.% Si) and at 97 °C on the Si-rich side (65 at.% Si), with an orthorhombic, $\alpha GdSi_2$-type low-temperature modification; they did not identify the high-temperature form, designated $\beta NdSi_x$ in this evaluation. The allotropic transformation temperature at the Si-rich limit (66.79 at.% Si) has been calculated to be 7.5 °C, using a linear extrapolation of the allotropic transformation data of [84Ere]. The high-temperature modification is indicated to be tetragonal, $\alpha ThSi_2$-type, based on the data of [68Ram]. [60Bin] noted that the melting temperature of

Fig. 1 Assessed Nd-Si Phase Diagram



A.B. Gokhale, A. Munitz, and G.J. Abbaschian, 1989.

Fig. 2 Schematic of the Catatectic (Inverse Peritectic) Reaction βNd ↔ α + L



A.B. Gokhale, A. Munitz, and G.J. Abbaschian, 1989.

"$NdSi_2$" is 1525 °C. In the present evaluation, the phase field of $NdSi_x$ was drawn to take this into account.

- Three eutectic reactions occur—between (Nd) and Nd_5Si_3 at 792 °C and 12.5 at.% Si, between NdSi and $NdSi_x$ at 1577 °C and 56 at.% Si, and between $NdSi_x$ and (Si) at 1197 °C and 83 at.% Si.

In addition, in this evaluation, the melting temperatures of the pure components have been revised to conform with the currently accepted values [86Gsc]. A catatectic (inverse peritectic) reaction involving the α ↔ β transformation of Nd has been included: [84Ere] indicated an allotropic transformation temperature for Nd of 837 °C, which is significantly different from the currently accepted value of 863 °C. The catatectic reaction, shown schematically on an expanded scale in Fig. 2, indicates a 26 °C depression in the allotropic transformation temperature of Nd due to the addition of Si.

The Nd-Si liquidus was determined reliably by [84Ere]. Because no thermodynamic data on the properties of the liquid solution are available in the literature, they were assessed in this evaluation using the experimental solubility data of [84Ere]; the mixing process was found to be slightly endothermic.

The mutual solid solubility limits of Si and Nd have not been reported. Based on the interaction of Si with other rare earths, the solubilities are probably negligible, as indicated in Fig. 1.

Nd-Si

Table 1 Monovariant and Invariant Nd-Si Equilibria

Reaction	Compositions of the respective phases, at.% Si			Temperature, °C	Reaction type
$L \leftrightarrow \beta Nd$		0		1021 (a)	Melting point
$\beta Nd \leftrightarrow \alpha Nd$		0		863 (a)	Allotropic transformation
$(\beta Nd) \leftrightarrow (\alpha Nd) + L$	2	0	10.5	837 (b)	Catatectic
$L \leftrightarrow (\alpha Nd) + Nd_5Si_3$	12.5	0	37	792	Eutectic
$L + Nd_5Si_4 \leftrightarrow Nd_5Si_3$	31.6	44.45	37.5	1447	Peritectic
$L + NdSi \leftrightarrow Nd_5Si_4$	36.3	50	44.45	1567	Peritectic
$L \leftrightarrow NdSi$		50		1677	Congruent point
$L \leftrightarrow NdSi + \beta NdSi_x$	56	50	64	1577	Eutectic
$NdSi + \beta Nd_2Si_3 \leftrightarrow Nd_3Si_4$	50	60	57.14	1397	Peritectoid
$NdSi + \beta NdSi_x \leftrightarrow \beta Nd_2Si_3$	50	64	60	1507	Peritectoid
$\alpha Nd_2Si_3 \leftrightarrow \beta Nd_2Si_3$		60		527	Allotropic transformation
$L \leftrightarrow \beta NdSi_x$		65.4		1757	Congruent point
$L \leftrightarrow \beta NdSi_x + (Si)$	83	66.79	100	1197	Eutectic
$\alpha NdSi_x \leftrightarrow \beta NdSi_x$		62 to 66.79		147 to 7.5	Allotropic transformation
$L \leftrightarrow Si$		100		1414 (c)	Melting point

From [84Ere]. **(a)** [86Gsc]. **(b)** This work. **(c)** [Melt].

Table 2 Nd-Si Crystal Structure Data

Phase	Composition, at.% Si	Pearson symbol	Space group	Strukturbericht designation	Prototype
βNd (a)	0	$cI2$	$Im\bar{3}m$	$A2$	W
αNd (b)	0	$hP4$	$P6_3/mmc$	$A3'$	αLa
Nd_5Si_3	$\sim$37 to $\sim$38	$tI32$	$I4/mcm$	$D8_1$	Cr_5B_3
Nd_5Si_4	44.55	...	$P4_12_12$	...	Zr_5Si_4
$NdSi$	50	$oP8$	$Pnma$	$B27$	FeB
Nd_3Si_4	57.14	...	...	...	...
αNd_2Si_3	60	$hP3$	$P6/mmm$	$C32$	AlB_2
βNd_2Si_3	60	...	...	...	...
$\alpha NdSi_x$	64 to 66.79	...	$Imma$	...	$\alpha GdSi_2$
$\beta NdSi_x$	64 to 66.79	$tI12$	$I4_1/amd$	C_c	$\alpha ThSi_2$
Si	100	$cF8$	$Fd\bar{3}m$	$A4$	C(diamond)

(a) From 1021 to 863 °C. **(b)** From 863 °C.

Table 3 Nd-Si Lattice Parameter Data at 24 °C

Phase	Composition, at.% Si	Lattice parameters, nm a	b	c	References Primary	Supplementary
BNd	0	0.413	...	...	[86Gsc] (a)	
αNd	0	0.36582	...	1.17966	[86Gsc]	[King1]
Nd_5Si_3	$\sim$37	0.770(5)	...	1.370(1)	[68Ram]	
	37.5	0.7674	...	1.3852	[84Ere]	[69May, 72 May]
		0.7787	...	1.373	[72May] (b)	
	$\sim$38	0.7745(5)	...	1.383(1)	[68Ram]	
Nd_5Si_4	44.45	0.7843	...	1 4818	[84Ere]	[67Smi, 68Ram]
NdSi	50	0.8756(5)	0.32920(3)	0.5881(3)	[66Hoh]	[64Gla, 65Par, 68Ram, 84Ere]
Nd_3Si_4	57.14	...	...	...		
αNd_2Si_3	60	0.3940(5)	...	0.4258(5)	[68Ram]	[84Ere]
βNd_2Si_3	60	...	...	...		
$\alpha NdSi_x$	64	0.4133	0.4099	1.3731	[84Ere]	
	65	0.4176	0.4145	1.3599	[84Ere]	
	66.67	0.418	0.415	1.356	[60Bin]	[67May]
$\beta NdSi_x$	66.67	0.4162(5)	...	1.358(1)	[67Ram]	[51Bra, 68Ram]
Si	100	0.54306	...	...	[King1]	

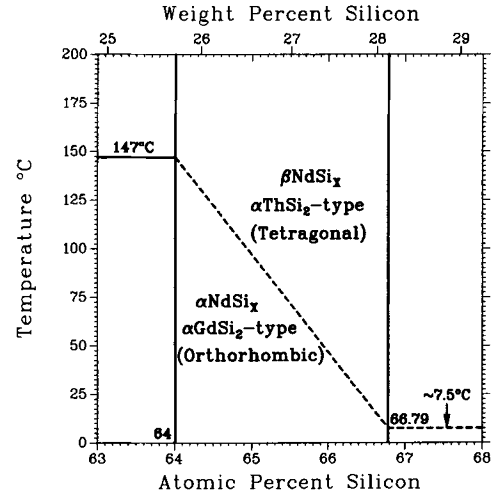
(a) Measurement at 883 °C. **(b)** Measurements at 280 °C.

Table 4 Crystal Structure and Lattice Parameter Data for $NdSi_x$ ($1.63 \le x \le 2.01$)

Prototype	Lattice parameters, nm			Cell volume, nm^3	Comment	Reference
	a	*b*	*c*			
$\alpha ThSi_2$ (a)	0.4111	...	1.356	0.22917	At 66.67 at.%Si	[51Bra]
	...	...	...	...	At 66.67 at.% Si	[58Mat]
	0.4162	...	1.358	0.23524	At 66.67 at.% Si	[67Ram]
	...	...	...	...	At 66.67 at.% Si	[68May] (c)
$\alpha GdSi_2$ (b)	0.418	0.415	1.356	0.23523	At 66.67 at.%Si	[60Bin]
	0.417	0.413	1.365	0.23508	At 66.67 at.% Si	[67May]
	0.4125	0.4095	1.371	0.23159	<66.67 at.% Si	[68Ram]
	0.4176	0.4145	1.3599	0.23539	At 65 at.% Si	[84Ere]
	0.4133	0.4099	1.3731	0.23262	At 64 at.% Si	[84Ere]

(**a**) Tetragonal. (**b**) Orthorhombic or distorted $\alpha ThSi_2$. (**c**) Noted that the structure is $\alpha ThSi_2$ type at 1600 °C.

Fig. 3 Schematic of the $NdSi_x$ Phase Field and Allotropic Transformation



A.B. Gokhale, A. Munitz, and G.J. Abbaschian, 1989.

Intermediate Phases

Physical properties for $NdSi_x$ ($NdSi_2$) have been reported in the literature. The phase, with electrical resistivity of 27 μΩ-cm, and a microhardness of 698 ± 10 kg/mm^2[65Sam, 66Dvo2] does not exhibit a superconducting transition down to 1 K [58Mat]. [72May] reported thermal expansion coefficients for the phase as follows:

$$\alpha_a = 9.8 \times 10^{-6}/K$$

and

$$\alpha_c = 11.0 \times 10^{-6}/K$$

where α_a and α_c are the thermal expansion coefficients in the *a* and *c* directions, respectively.

Crystal Structures and Lattice Parameters

Selected Nd-Si crystal structure and lattice parameter data are summarized in Tables 2 and 3. The data are taken from references listed under "primary reference," chosen on the basis of thoroughness of investigation, listing of diffraction data, and agreement with other investigations; other pertinent reference are listed under "supplementary references."

The crystal structure and lattice parameter(s) of Nd_3Si_4 have not been determined. The reported data for other intermediate phases show good agreement, except in two instances: (1)For Nd_5Si_3, [69Nar] reported a wrong prototype (Mn_5Si_3, instead of Cr_5B_3), and thus a wrong space group. Their lattice parameter data are therefore not considered in this evaluation; and (2)The crystal structure and lattice parameter data for $NdSi_x$ are somewhat conflicting with regard to the crystal type present, and they show a variation in the lattice parameters for the same crystal type. The conflict apparently stems from three factors—$NdSi_x$ exhibits a rather wide homogeneity range, the allotropic transformation temperature changes with Si contents (Fig. 3), and the transformation is of a displacive type and thus is difficult to measure accurately [59Per].

It should be noted that the structural change in $NdSi_x$ from $\alpha GdSi_2$ type to $\alpha ThSi_2$ type is accompanied by only small changes in the volume of the unit cell. Further, the *a* and *b* dimensions for the $\alpha GdSi_2$ type are only slightly different. Also, as mentioned above, if the allotropic transformation temperature data of [84Ere] are extrapolated linearly to the Si-rich limit of the phase, a transformation temperature of 7.5 °C is obtained. Thus, alloys synthesized in the Si-rich limit would exhibit the high-temperature, $\alpha ThSi_2$-type structure at room temperature. For this reason, we have designated the low-temperature modification of the phase $\alpha GdSi_2$ type (distorted $\alpha ThSi_2$) and the high-temperature modification as $\alpha ThSi_2$ type. A similar behavior is also observed in other RE-Si systems.

Thermodynamics

The present evaluators are unaware of any thermodynamic investigation of either the liquid solution or the intermediate phases in the system. In this evaluation, the thermodynamic properties of the liquid were assessed using the experimental solubility data of [84Ere] and the Gibbs energies of fusion for the pure components. The enthalpy of mixing in the liquid can be represented by:

$$\Delta_{\text{mix}}H = X_{\text{Nd}}(1 - X_{\text{Nd}})(-42.49 + 285.18X_{\text{Nd}} - 385.72X^2_{\text{Nd}} + 160.46X^3_{\text{Nd}} \quad \text{kJ/mol}$$

where X_{Nd} is the atomic fraction of Nd.

According to this calculation, the liquid solution is slightly endothermic, with a maximum heat absorption of 6.04 kJ/mol at 54.3 at.% Nd. Because these results are based solely on the experimental solubility data of [84Ere], they should be used with caution. Also, in other RE-Si systems, liquid solutions exhibit a strongly exothermic behavior.

The Gibbs energies of fusion for the pure components used in the calculation were represented as a function of temperature in the following form:

$$\Delta_{\text{fus}}G(\text{Nd}) = 1673.8 + 28.99\,T - 4.226\,T\ln T \quad \text{kJ/mol}$$

and

$$\Delta_{\text{fus}}G(\text{Si}) = 48\,527 + 0.497\,T + 1.93 \times 10^{-3}\,T^2 - 4.372\,T\ln T - 1.77 \times 105\,T^{-1} \quad \text{kJ/mol}$$

where T is in K. The heat capacities and heats of fusion for the pure components are taken from [77Bar].

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* Indicates a key paper.

# Indicates the presence of a phase diagram.

Nd-Si evaluation contributed by **A.B. Gokhale, A. Munitz,** and **G.J. Abbaschian,** Department of Materials Science and Engineering, University of Florida, Gainesville, FL 32611. This work was supported by ASM International under grant No. FG 101-1. Thermodynamic calculations were made using the F*A*C*T computer program at the McGill University, Montreal, Quebec, Canada. The evaluators wish to thank Dr. K.A. Gschneidner, Jr., Director, Rare Earth Information Center, Iowa State University, for his help in providing some of the literature sources. Literature searched through 1984. Professor Abbaschian is the ASM/NIST Data Program Category Editor for binary silicon alloys.

The Hf-Li (Hafnium-Lithium) System

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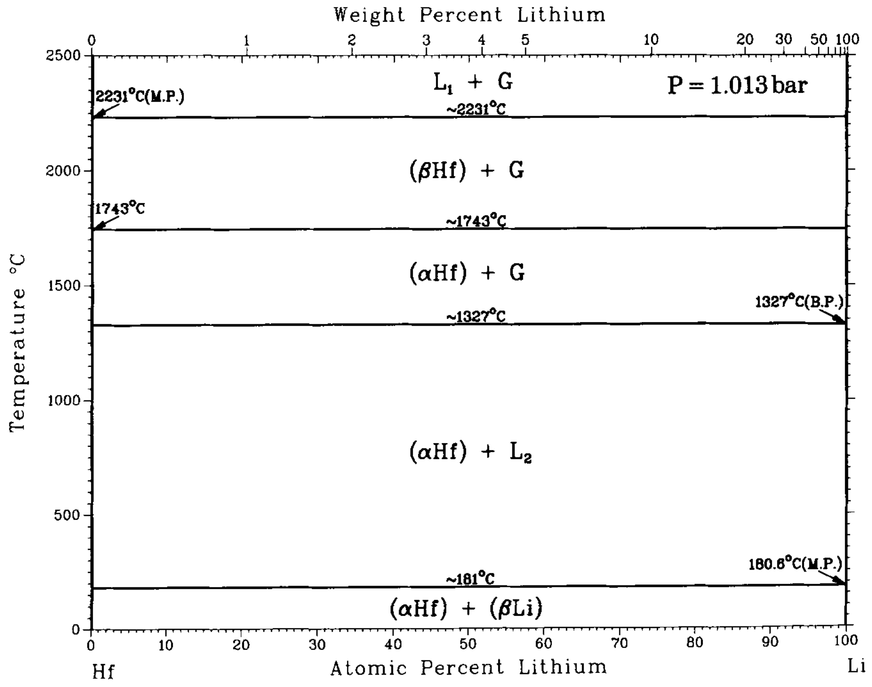
Equilibrium Diagram

The assessed Hf-Li phase diagram is shown in Fig. 1. There are no published data for the Hf-Li phase diagram. By analogy with Li-Ti and Li-Zr and with the other alkali metal-group IV A systems, it is probable that the system is almost completely immiscible in both the solid and liquid states.

If the solubilities are very limited, it follows from thermodynamic considerations that the univariant temperatures in the phase diagram are virtually identical

Fig. 1 Assessed Hf-Li Phase Diagram



C.W. Bale, 1989.