The Ni-Pr (Nickel-Praesodymium) System

Y.Y. Pan and P. Nash
Illinois Institute of Technology

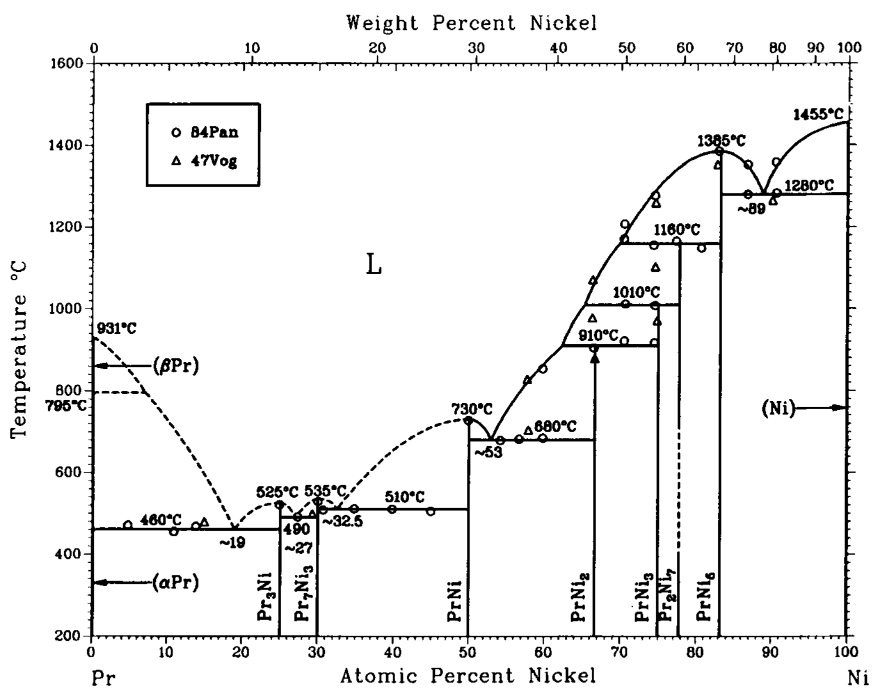
Equilibrium Diagram

The assessed Pr-Ni phase diagram (Fig. 1) is based primarily on the differential thermal analysis (DTA) and X-ray analysis data of [47Vog] and [84Pan]. It consists of seven intermetallic compounds—Pr_3Ni, Pr_7Ni_3, PrNi, $PrNi_2$, $PrNi_3$, Pr_2Ni_7, and $PrNi_5$. $PrNi_2$, $PrNi_3$, and Pr_2Ni_7 form by peritectic reactions, and the others are congruently melting compounds; five eutectic reactions occur. Invariant reaction

Table 1 Invariant Reactions in the Pr-Ni System

Reaction	Compositions of the respective phases, at.% Ni			Temperature, °C	Reaction type
L ↔ βPr		0		931	Melting point
βPr ↔ αPr		0		795	Allotropic
L ↔ (αPr) + Pr_3Ni	~19	0	25	460	Eutectic
L ↔ Pr_3Ni		25		525	Congruent
L ↔ Pr_3Ni + Pr_7Ni_3	~27	25	30	490	Eutectic
L ↔ Pr_7Ni_3		30		535	Congruent
L ↔ Pr_7Ni_3 + PrNi	~32.5	30	50	510	Eutectic
L ↔ PrNi		50		730	Congruent
L ↔ PrNi + $PrNi_2$	~53	50	66.7	680	Eutectic
L + $PrNi_3$ ↔ $PrNi_2$	~62	75	66.7	910	Peritectic
L + Pr_2Ni_7 ↔ $PrNi_3$	~65	77.8	75	1010	Peritectic
L + $PrNi_5$ ↔ Pr_2Ni_7	~70	83.3	77.8	1160	Peritectic
L ↔ $PrNi_5$		83.3		1385	Congruent
L ↔ $PrNi_5$ + (Ni)	~89	83.3	100	1280	Eutectic
L ↔ Ni		100		1455	Melting point

Fig. 1 Assessed Pr-Ni Phase Diagram



Y.Y. Pan and P. Nash, 1989.

temperatures and compositions are summarized in Table 1. There is no solid solubility of either metal in any of the compounds. The terminal solid solutions are also very restricted, but the extent has not been clearly established.

[47Vog] first studied this system using Pr with 98 to 99 wt.% purity. No information on Ni purity was given. The diagram was established on data obtained from only nine alloys, which were selected at critical compositions on the basis of the similarity of Ni-Pr to the La-Ni and Ce-Ni systems. [47Vog] reported four compounds—Pr_3Ni, PrNi, $PrNi_2$, and $PrNi_5$. The existence of $PrNi_3$ and $PrNi_4$ was uncertain. His diagram cannot be considered accurate, because only a limited number of samples were used in the thermal analysis.

In view of the X-ray data for Ce_2Ni_7 [59Cro], [61Gsc] proposed that the true composition of $PrNi_4$ should be Pr_2Ni_7. This was confirmed by [70Bus] and [71Tay] using X-ray analysis. [70Bus] suggested that there are two modifications of Pr_2Ni_7. The high-temperature form is hexagonal, and the low-temperature form is rhombohedral, but the transformation temperature was not determined. X-ray diffraction (XRD) has also confirmed the existence of Pr_3Ni [67Lem1], PrNi [63Dwi, 65Dwi, 64Abr, 64Wal], $PrNi_2$ [60Wer, 71Tay], and $PrNi_5$ [59Wer, 61Dwi]. [47Vog] suggested that $PrNi_2$ decomposes peritectically at 880 °C but [60Wer] did not observe any transistion between room temperature and 880 °C in their DTA study. [66Kis] reported a Pr-Ni compound with Fe_3Th_7 structure type. It was investigated by [73Olc] using metallographic and XRD techniques on alloys prepared in a tantalum furnace or in an arc melting furnace from 99.9 wt.% Pr and 99.998 wt.% Ni. The occurrence of Pr_7Ni_3 was ascertained, and the lattice parameters were measured.

[84Pan] investigated this system using DTA and XRD of samples prepared by induction melting under purified argon of 99.9 wt.% Pr and 99.99 wt.% Ni. Each sample was remelted several times, then homogenized by appropriate thermal treatments (Table 2). Seven previously reported compounds were confirmed. The diagram of [84Pan] is similar to that of a previous evaluation [61Gsc], but the temperatures and compositions of the reactions are rather different. The data of [84Pan] are accepted in Fig. 1, because they used higher-purity starting metals than [47Vog].

The melting points of Pr and Ni are 931 and 1455 °C, respectively [Melt]. The temperature of the allotropic transformation $\alpha Pr \leftrightarrow \beta Pr$ is 795 °C [86Gsc]. The effect of Ni on this transformation is not known. [84Pan] investigated samples with compositions between 50 and 67 at.% Ni and found two peaks (~680 and ~700 °C) on the DTA curves of some samples. The XRD pattern showed some extra lines, but [84Pan] did not obtain enough data to determine if another phase exists in this region.

Table 2 Thermal Treatment of Pr-Ni alloys

Composition, at.% Ni	Temperature, °C	Time, days
0 to 45	400	30
45 to 75	500	30
75 to 100	800	30

From [84Pan].

Crystal Structures and Lattice Parameters

Pr-Ni crystal structures and lattice parameters are given in Tables 3 and 4.

Thermodynamics

The heat capacity (C_p) and derived thermodynamic properties of $PrNi_2$ and $PrNi_5$ are summarized in Table 5. The C_p data for $PrNi_2$ are shown in Fig. 2, which shows that heat capacity of the compound is much larger than that of its constituent elements.

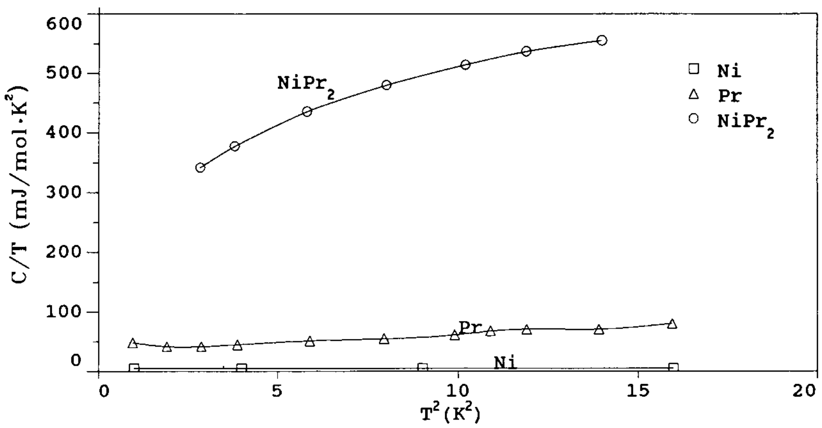
The specific heat of $PrNi_5$ was measured over the temperature range 1.6 to 4 K [71Nas]. The results can be represented as:

Table 3 Pr-Ni Crystal Structure Data

Phase	Composition, at.% Ni	Pearson symbol	Space group	Strukturbericht designation	Prototype	Reference
βPr(a)	0	*cI*2	*Im*3*m*	*A*2	W	[86Gsc]
αPr(b)	0	*hP*4	*P*6₃/*mmc*	*A*3′	αLa	[86Gsc]
Pr_3Ni	25.0	*oP*16	*Pnma*	$D0_{11}$	Fe_3C	[67Lem1]
Pr_7Ni_3	30.0	*hP*20	$P6_3mc$	$D10_2$	Fe_3Th_7	[73Olc]
PrNi	50.0	*oC*8	*Cmcm*	B_f	CrB	[64Wal, 65Dwi]
$PrNi_2$	66.7	*cF*24	*Fd*3*m*	*C*15	Cu_2Mg	[47Vog]
$PrNi_3$	75.0	*hR*24	*R*3*m*	...	$PuNi_3$	[67Pac]
Pr_2Ni_7	77.8	*hP*36	$P6_3/mmc$	...	Ce_2Ni_7(c)	[70Bus]
		*hR*54	*R*3*m*	...	Gd_2Ni_7(d)	[70Bus]
$PrNi_5$	83.3	*hP*6	*P*6/*mmm*	$D2_d$	$CaCu_5$	[59Wer]
Ni	100	*cF*4	*Fm*3*m*	*A*1	Cu	[King1]

(a) From 931 to 795 °C. (b) From 745 °C. (c) High-temperature form. (d) Low-temperature form.

Fig. 2 Heat Capacity of $PrNi_2$



From [73Wal]. Y.Y. Pan and P. Nash, 1989.

Table 4 Pr-Ni Lattice Parameter Data

Phase	Composition, at.% Ni	Lattice parameters, nm a	b	c	Comment	Reference
βPr	0	0.413	...	...	At >795 °C	[86Gsc]
αPr	0	0.36721	...	1.18326	At 25 °C	[86Gsc]
Pr_3Ni	25.0	0.707	0.996	0.649	...	[67Lem1]
Pr_7Ni_3	30.0	0.9904	...	0.6322	...	[[73Olc]
PrNi	50.0	0.3816	1.0503	0.4354	...	[65Dwi]
		0.3817	1.0501	0.4347	...	[64Abr]
		0.379	1.039	0.433	...	[64Wal]
$PrNi_2$	66.7	0.720	...	...	...	[47Vog]
		0.7285	...	...	...	[60Wer]
		0.7274	...	...	...	[71Tay]
$PrNi_3$	75.0	0.5035	...	2.432	...	[70Bus]
		0.503	...	2.501	...	[67Pac]
Pr_2Ni_7	77.8	0.5015	...	2.444(a)	...	[70Bus]
		0.501	...	2.423	...	[71Tay]
		0.5015	...	3.664(b)	...	[70Bus]
$PrNi_5$	83.3	0.4958	...	0.3980	...	[59Wer]
		0.4948	...	0.3973	...	[47Vog]
		0.4964	...	0.3975	...	[61Dwi]
Ni	100	0.35241	...	...	...	[King1]

(a) High-temperature form. **(b)** Low-temperature form.

$$C_p = \gamma T + \beta T^3$$

where the electronic specific heat coefficient γ is 37.02 + 0.16 mJ/mol · K^4. The Debye temperature (θ_D) of 333.5 K was estimated by [71Nas] using the expression:

$$\beta = (12/5)\pi^4 kN/\theta_D{}^3$$

where k is Boltzmann's constant and N is Avogadro's number.

The enthalpies (ΔH) of the transition L ↔ βPr and βPr ↔ αPr are 6890 and 3170 J/mol, respectively [83Cha].

Magnetism

The magnetic behaviors of the Pr-Ni compounds are listed in Table 6. The temperature dependence of the magnetization of $PrNi_5$ is shown in Fig. 3.

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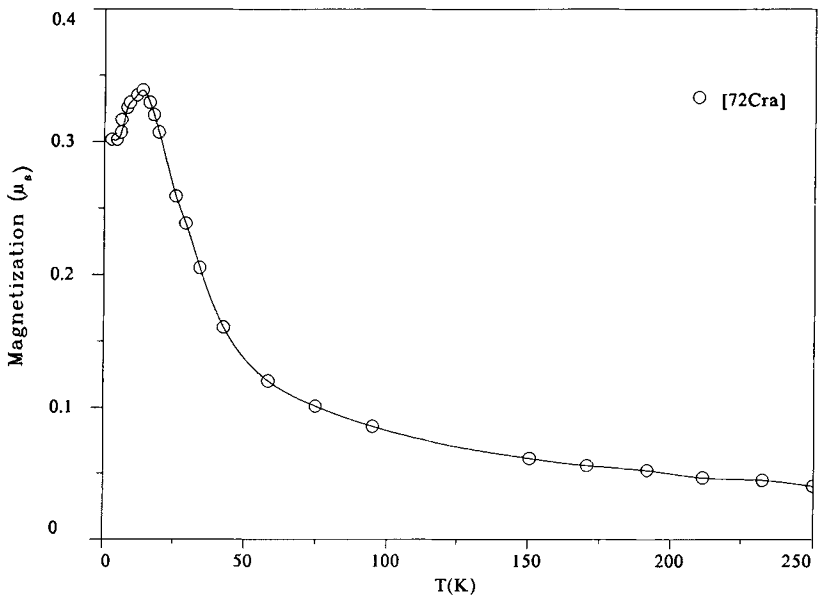
Fig. 3 Temperature Dependence of Magnetization of PrNi5



From [72Cra]. Y.Y. Pan and P. Nash, 1989.

Table 6 Magnetic Characteristics of Ni-Pr Compounds

Compound	Paramagnetic Debye temperature, K	Paramagnetic Effective moment, μ_B/Pr	State type	Curie temperature, K	Ordered moment, μ_B/Pr	State type	Reference
Pr_3Ni	−24	3.7	Curie-Weiss	...	...	Antiferromagnetic	[68Fer]
Pr_7Ni_3	−2	3.6	Curie-Weiss(a)	...	...	...	[66Kis]
PrNi	23	3.9	Curie-Weiss	22	2.26	Ferromagnetic	[64Wal,64Abr]
$PrNi_2$	4	3.57	Curie-Weiss(a)	...	...	...	[66Far, 68Mad]
$PrNi_3$	...	...	...	20	1.57	Ferromagnetic	[67Pac]
Pr_2Ni_7	...	...	...	85	4.36(b)	Ferromagnetic	[67Lem2]

From [73Wal]. **(a)** Exhibits Van Vlek paramagnetism. **(b)** Per formula unit of Pr_2Ni_7.

Table 5 Heat Capacities and Derived Thermodynamic Properties of Pr_2Ni_2 and $PrNi_5$ (a)

Property	$PrNi_2$	$PrNi_5$
Heat capacity (C_p)	77.62	162.20
Enthalpy (H–H_0)/T	57.78	109.98
Entropy (S)	136.58	230.14
Gibbs energy −(G–H_0)/T	78.81	120.16
Entropy at fusing (ΔS_f)	3.66	7.61

From [73Wal]. **(a)** at 298.15 K in J/mol·K.

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

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