

Magnetic and Structural Properties of Transition Metal Substituted MnP. IV. $Mn_{1-t}Ni_tP$

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The pseudo-binary $Mn_{1-t}Ni_tP$ phase is investigated by X-ray and neutron diffraction as well as magnetic susceptibility measurements. The MnP type structure prevails up to $t \approx 0.65$, where a multi phase region ($\sim 0.65 < t \leq 1.00$) with non-equilibrium states takes over. The ferromagnetic (F) state of MnP extends to $0.10 < t < 0.20$ of $Mn_{1-t}Ni_tP$, whereas the existence range of the helimagnetic (H_c) state only covers a very narrow ternary range ($0.00 \leq t < \sim 0.002$). A magnetic two phase region ($\sim 0.002 < t < \sim 0.015$) separates the H_c and F phases.

Among the monophosphides of the 3d metals, TiP and NiP distinguish themselves in that they neither take the NiAs nor the MnP type crystal structure. The detailed discussion by Larsson¹ of structural relationships shows that the atomic arrangements of the NiP and MnP types can be regarded as distorted variants of the more symmetric NiAs type structure. The number of short metal – metal distances per metal atom increases, e.g., from two in the normal NiAs type (VP represents an exception²) to three in NiP and four in the (fully transformed^{3,4}) MnP type. The unique structural position of NiP renders studies of its mutual solid solubilities with the other 3d monophosphides interesting.

The present paper gives an account of structural and magnetic properties of $Mn_{1-t}Ni_tP$. The earlier studies^{5–8} on the $Mn_{1-t}T_tP$ phases with $T=V, Fe$ and Co have revealed a number of interesting phenomena over the wide solid solution ranges of these phases. The para- (P), ferro- (F) and helimagnetic (H_c) states of MnP (cf., e.g., Ref. 6) extend into the ternary regions, and for $T=V$ ^{5,7} and Fe ^{5,8} the P, F and H_c phases

meet in a triple point. The Curie temperature (T_C) and the saturation magnetic moment (μ ; at 4.2 K) is found⁵ to decrease approximately linearly with the difference in the number of (outer) electrons ($\Delta n = n_{Mn_{1-t}T_tP} - n_{MnP}$). With $T=V, Cr, Fe$ and Co the earlier studies have been theoretically limited to $|\Delta n| \leq 2$, in practice to $|\Delta n| \leq 0.6$. For $T=Ni$ the theoretical limit is extended to $|\Delta n| \leq 3$.

On this background there are accordingly a number of open questions connected with $Mn_{1-t}Ni_tP$ and the present contribution aims at elucidating some of these.

EXPERIMENTAL

The ternary, small and large scale, samples of $Mn_{1-t}Ni_tP$ were made from initial batches of MnP and “NiP”. The preparational procedure for MnP followed Ref. 6, where also the purity of the starting materials of Mn and P is given. Turnings from 99.995 % Ni rods (Johnson, Matthey & Co.) were used in the syntheses of “NiP”. “NiP” denotes a sample with the said nominal composition. Since NiP is a high temperature phase (stable above $\sim 850^\circ C$ ¹) it was decided not to put any effort into the isolation of this compound which would decompose during the syntheses of the ternary samples anyway. Instead it was aimed at a mixture of Ni_5P_4 and NiP_2 which proved perfectly adequate for the following preparations of the ternary samples. Stoichiometric 1:1 quantities of Ni and P were heated in evacuated, sealed, double quartz tubes placed in horizontally positioned furnaces. The temperature was increased ($3 \times 50^\circ C$ per d) to $875^\circ C$, kept there for 1 d and cooled to room temperature over 1 d. The thus obtained “NiP” was carefully crushed and checked by the powder X-ray (Guinier) technique.

Weighed amounts of MnP and "NiP", in proportions appropriate to the desired ternary compositions, were subjected to a first heat treatment at 900 °C for 7 d. The samples were carefully ground before subjected to one or more further heat treatments. Various annealing conditions were tried in this part of the preparational procedure in attempts to obtain single phase samples in the NiP rich region of the MnP–NiP system. However, for $t > \sim 0.65$ of $\text{Mn}_{1-t}\text{Ni}_t\text{P}$ all these endeavours (numerous annealing temperatures between 600 and 900 °C, varied heating times and different quenching and slow cooling conditions) were in vain and the final products proved always to be multi phase samples.

All samples were examined by powder X-ray (Guinier) diffraction at room temperature, and selected samples also by metallographic methods to test and/or ensure homogeneity. Experimental details concerning powder X-ray and neutron diffraction, magnetic susceptibility and differential thermal analysis (DTA) are given in Ref. 9. The nuclear neutron scattering lengths (in 10^{-12} cm) $b_{\text{Mn}} = -0.37$, $b_{\text{Ni}} = 1.03$ and $b_{\text{P}} = 0.51$ were taken from Ref. 10, and the magnetic form factor for Mn^{2+} from Ref. 11.

RESULTS AND DISCUSSION

(i) *Homogeneity ranges and atomic arrangement.* Since MnP and NiP take rather different crystal structures, there must be one (or more) miscibility gap(s) in the MnP–NiP system. As indicated in Fig. 1, the situation is even more complicated in that all attempts (*cf.* the experimental section) to prepare $\text{Mn}_{1-t}\text{Ni}_t\text{P}$ samples with nominal composition $\sim 0.65 < t \leq 1.00$ invariably resulted in a mixture of several phases. The same problem was encountered for $t = 0.50$ and 0.60 , but could here be overcome by the use of repeated heat treatments. Powder X-ray (Guinier) diagrams show that the bulk of the multi phase samples are composed of $\text{Mn}_{1-t}\text{Ni}_t\text{P}$ with $t \approx 0.6$, NiP_2 and Ni_5P_4 . Moreover, even NiP was not obtained in this study. From Larsson's paper¹ it is evident that NiP is a high temperature phase which is difficult to attain. However, to our surprise even spot traces of NiP could not be registered on high temperature X-ray photographs of mixtures of NiP_2 and Ni_5P_4 with nominal composition NiP.

Fig. 1 shows also the room temperature unit cell dimensions of $\text{Mn}_{1-t}\text{Ni}_t\text{P}$ as function of the compositional parameter t . The continuous varia-

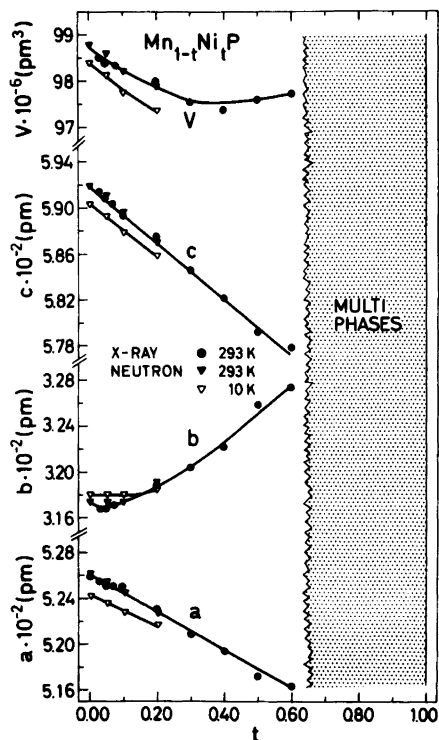


Fig. 1. Unit cell dimensions $\text{Mn}_{1-t}\text{Ni}_t\text{P}$ versus t at 10 and 293 K. Legends to symbols are given on the illustration. Calculated error limits do not exceed the size of symbols. ($1 \text{ \AA} = 10^2 \text{ pm}$.) Concerning the multi phase region see text.

tions in all unit cell dimensions with t demonstrate the solid solubility up to $t \approx 0.60$.

The powder neutron (and X-ray) diffraction data show unambiguously that Mn and Ni are long range distributed at random over the metal sub-lattice of an MnP type crystal structure. The unit cell dimensions and positional parameters as derived by Rietveld analyses of the powder neutron diffraction data, are listed in Table 1. The positional parameters for $\text{Mn}_{1-t}\text{Ni}_t\text{P}$ (Table 1) are, consistent with the findings^{6-8,12,13} for other $\text{Mn}_{1-t}\text{Ti}_t\text{P}$ phases, constant within two calculated standard deviations (*cf.* Ref. 7).

The compositional dependences of the unit cell dimensions of $\text{Mn}_{1-t}\text{Ni}_t\text{P}$ for $0.00 \leq t \leq 0.20$ at 10 K are also included in Fig. 1. $\text{Mn}_{1-t}\text{Ni}_t\text{P}$ concurs with other $\text{Mn}_{1-t}\text{Ti}_t\text{P}$ phases examined so far^{6-8,12,13} in that its b axis is expanded between 293 and 10 K. The interval where the b axis of

Table 1. Unit cell dimensions and positional parameters with standard deviations for $Mn_{1-t}Ni_tP$ as derived by Rietveld analysis of powder neutron diffraction data. Space group $Pnma$; Mn/Ni in 4c and P in 4c. (Nuclear R_p -factors ranging between 0.02 and 0.06; magnetic R_m -factors ranging between 0.03 and 0.07; profile R_p -factors ranging between 0.08 and 0.15; 20–25 nuclear reflections.)

t	T (K)	a (pm)	b (pm)	c (pm)	x_T	z_T	x_P	z_P
0.01	293	525.85(3)	317.31(2)	591.69(3)	0.0051(13)	0.1953(8)	0.1902(8)	0.5692(6)
	60	524.07(3)	318.07(3)	590.27(3)	0.0041(12)	0.1937(8)	0.1900(7)	0.5696(6)
	10	523.95(3)	318.28(2)	590.13(3)	0.0021(12)	0.1925(9)	0.1899(7)	0.5682(6)
0.05	293	525.52(4)	317.43(2)	591.25(4)	0.0049(27)	0.1986(27)	0.1874(14)	0.5700(9)
	10	523.58(8)	318.09(5)	589.23(9)	-0.0004(26)	0.1958(26)	0.1905(20)	0.5718(11)
0.10	293	524.52(5)	317.53(2)	589.68(5)	0.0066(28)	0.1954(28)	0.1891(16)	0.5692(9)
	10	522.81(4)	318.02(2)	587.84(5)	0.0051(18)	0.1992(14)	0.1878(8)	0.5714(6)
0.20	293	522.98(5)	318.95(2)	586.99(4)	-0.0021(20)	0.2008(21)	0.1910(8)	0.5719(5)
	10	521.86(6)	318.53(4)	585.79(5)	-0.0011(16)	0.1985(19)	0.1904(7)	0.5699(7)

$Mn_{1-t}Ni_tP$ is expanded ($0.00 \leq t \leq \sim 0.20$) matches the stability range of its F phase [see (iii)].

As seen from Fig. 1 the unit cell dimensions vary appreciably over the homogeneity range of the $Mn_{1-t}Ni_tP$ phase. This brings about a substantial decrease in c/b from 1.865 at $t=0.00$ to 1.766 at $t=0.60$, whereas ca only changes slightly (1.125 versus 1.119). Since $c/b \rightarrow \sqrt{3} = 1.73205\dots$ serves as a necessary, but not a sufficient condition for an $MnP \rightarrow NiAs$ type phase transition, it seemed pertinent to test the possibility of such a transition. $Mn_{0.50}Ni_{0.50}P$ was chosen for the purpose, and the unit cell dimensions versus temperature relationships for this composition are shown in Fig. 2. However, $Mn_{0.50}Ni_{0.50}P$ retains the MnP type structure up to 1150 K, which is close to its melting point of ~ 1200 K. (Other melting points estimated from DTA are ~ 1340 , ~ 1310 and ~ 1150 K for $t=0.30$, 0.40 and 0.60, respectively.)

(ii) *Magnetic susceptibility.* The reciprocal magnetic susceptibility versus temperature curves for $Mn_{1-t}Ni_tP$ with $0.00 < t \leq 0.40$ in Fig. 3 exhibit a gradual change in character. The straight lines

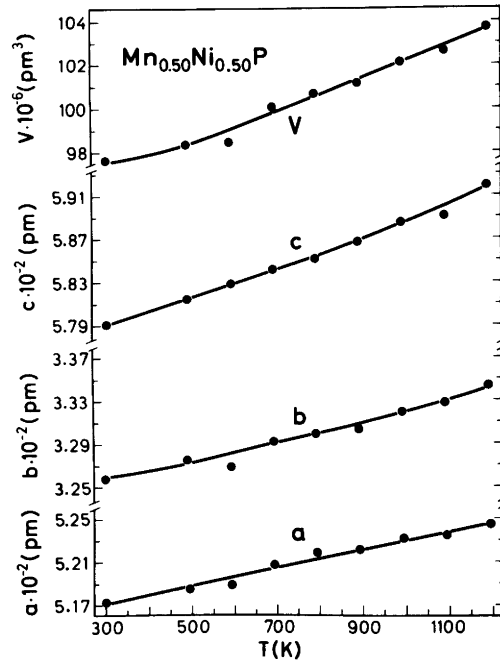


Fig. 2. Unit cell dimensions of $Mn_{0.50}Ni_{0.50}P$ as function of temperature. Calculated error limits do not exceed the size of symbols. ($1 \text{ \AA} = 10^2 \text{ pm}$.)

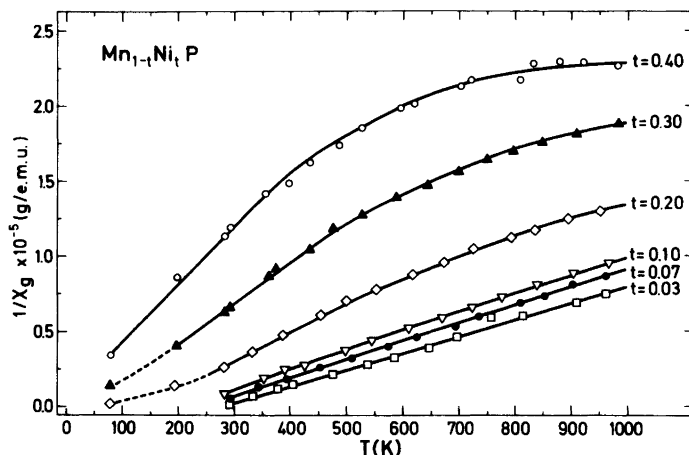


Fig. 3. Inverse magnetic susceptibility as function of temperature for $\text{Mn}_{1-t}\text{Ni}_t\text{P}$ with $t=0.03, 0.07, 0.10, 0.20, 0.30$ and 0.40 .

for substitution levels of Ni up to $t=0.10$ convert to slightly sigmoidally shaped curves for $t \geq 0.20$. This trend resembles the findings for other $\text{Mn}_{1-t}\text{T}_t\text{P}$ phases.^{6-8,12,13}

The paramagnetic moments ($\mu_{\text{eff}}=[8C_{\text{mol}}]^{1/2}$) and Weiss constants (θ), as derived from Curie-Weiss law [$\chi^{-1}=C^{-1}(T-\theta)$] regions of the $\chi^{-1}(T)$ curves (Fig. 3), are listed in Table 2. The table also includes the corresponding number of unpaired spins ($2S$) according to the "spin only" approximation [$\mu_{\text{eff}}=g[S(S+1)]^{1/2}$ with $g=2$].

θ , μ_{eff} and $2S$ decrease with increasing t , and $\text{Mn}_{1-t}\text{Ni}_t\text{P}$ resembles in this respect the other $\text{Mn}_{1-t}\text{T}_t\text{P}$ phases^{6-8,12,13} which we have studied. The resemblance also extends to an almost perfect match between the θ values (Table 2) and the Curie temperatures for the $\text{P} \rightleftharpoons \text{F}$ transition found by neutron diffraction [see (iii)]. The

relation between $2S$ and the ferromagnetic moments derived by neutron diffraction [see (iii)] is shown in Fig. 4. In line with the findings for other $\text{Mn}_{1-t}\text{Ni}_t\text{P}$ phases the paramagnetic $2S$ values are appreciably higher than the ordered moments, and the results trace out two approximately parallel lines which decline with increasing t . These aspects will be discussed further in relation to the corresponding data for all $\text{Mn}_{1-t}\text{T}_t\text{P}$ phases.¹³

(iii) *Magnetic phase diagram and structures.* The present neutron diffraction results confirm the existence of the F phase for $t=0.01, 0.05$ and 0.10 with, respectively, $T_C=283 \pm 5, 275 \pm 5$ and 234 ± 5 K and $\mu_F=1.37(5) \mu_B$ at 60 K, $\mu_F=1.34(8) \mu_B$ at 10 K and $\mu_F=1.01(5) \mu_B$ at 10 K. As for the other $\text{Mn}_{1-t}\text{T}_t\text{P}$ phases,^{6-8,12,13} the direction of the ferromagnetic moments is parallel to b .

Table 2. Weiss constant (θ), paramagnetic moment (μ_{eff}) and number of unpaired spins ($2S$) for $\text{Mn}_{1-t}\text{Ni}_t\text{P}$.

t	θ (K)	μ_{eff} (μ_B per T)	$2S$ (per T)
0.03	277 ± 5	2.53 ± 0.05	1.72 ± 0.04
0.07	253 ± 5	2.37 ± 0.05	1.58 ± 0.04
0.10	226 ± 5	2.32 ± 0.05	1.52 ± 0.04
0.20 ^a	152 ± 20	1.90 ± 0.20	1.15 ± 0.16
0.30 ^b	54 ± 20	1.58 ± 0.20	0.87 ± 0.16
0.40 ^c	-6 ± 20	1.33 ± 0.20	0.66 ± 0.16

^a For $250 < T < 550$ K. ^b For $200 < T < 500$ K. ^c For $80 < T < 350$ K.

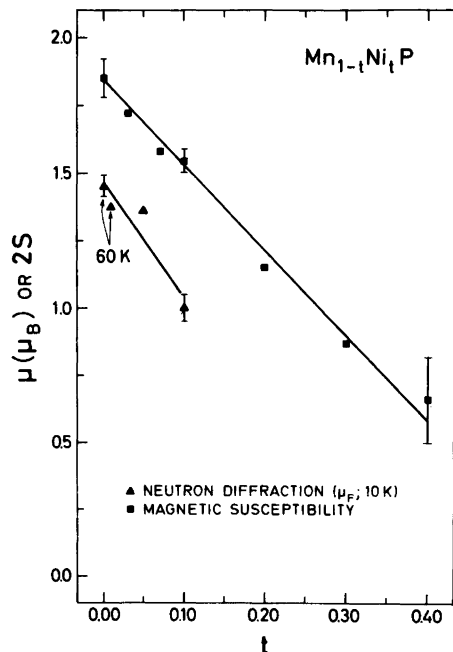


Fig. 4. Paramagnetic ("spin only") $2S$ values and ferromagnetic moments from neutron diffraction versus the compositional parameter t . Legends to symbols are given on the illustration. Bars represent estimated or calculated errors.

$Mn_{1-t}Ni_tP$ differs from the $Mn_{1-t}T_tP$ phases with $T=V$,⁷ Fe ,⁸ Co ,⁶ Mo ¹³ and W ¹³ in that the existence range of the H_c phase is very narrow ($0.00 \leq t < \sim 0.002$), and a magnetic two phase region ($\sim 0.002 < t < \sim 0.015$) separates the H_c and F phases. The latter inferences have been derived from the sample with $t=0.01$ which crystallographically is definitely single phase for $10 < T < 293$ K. $Mn_{0.99}Ni_{0.01}P$ is also magnetically single phase for $283 \pm 5 > T > 52 \pm 3$ K (where the former temperature limit corresponds to T_C and the latter to T_S for the H_c to F transition of a sample with estimated composition $t \approx 0.002$). A section of the magnetic phase diagram for $Mn_{1-t}Ni_tP$ which complies with the present results is shown in Fig. 5. The boundary of the F phase has not been precisely stipulated for $0.10 < t < 0.20$, but the T_C curve must go to zero in this interval since $Mn_{0.80}Ni_{0.20}P$ appears to be confined to the P state for $10 < T < 293$ K. (The neutron diffraction measurements for $t=0.20$ do not completely rule out the existence of an F state at 10 K, but

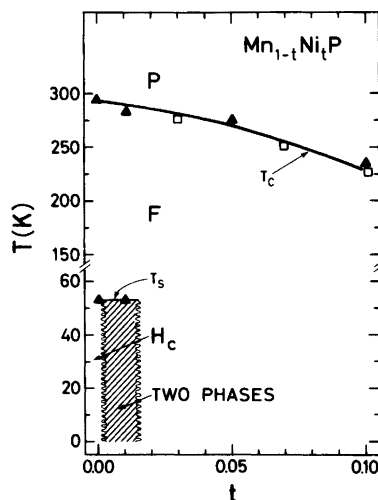


Fig. 5. Section of the magnetic phase diagram for $Mn_{1-t}Ni_tP$. Open symbols refer to θ values from magnetic susceptibility data, solid symbols to neutron diffraction data. Shaded area corresponds to a magnetic two phase region.

the ordered moment must in that case be very small, $\mu_F < 0.5 \mu_B$.) We expect that the F state of $Mn_{1-t}Ni_tP$ is replaced by a spin glass region (cf. Ref. 5) at higher substitution levels of Ni (viz. for $t > \sim 0.20$).

Due to the magnetic two phase nature of $Mn_{0.99}Ni_{0.01}P$ below 52 ± 3 K it is difficult to obtain reasonable estimates of the helimagnetic moment (μ_H) for the H_c of $Mn_{1-t}Ni_tP$ with $t \approx 0.002$. However, its spiral propagation vector (τ_c) is easily and accurately determined and $\tau_c/2\pi c^*$ values (uncertainty $\sim \pm 0.002$) of 0.110, 0.104, 0.102, 0.100, 0.099 and 0.099 are obtained for $T=10, 23, 29, 34, 40$ and 50 K, respectively. The phase angle $\phi_{1,2}$ between the spirals through atoms 1 and 2 (cf. Ref. 9) is estimated to be some $20 \pm 5^\circ$ and essentially temperature independent for $t \approx 0.002$.

Finally it may be mentioned that the data for the ferromagnetic state of $Mn_{1-t}Ni_tP$ cover a too narrow composition range to shed further light on the T_C and μ versus Δn relation⁵ referred to in the introduction.

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