Magnetic and Structural Properties of Transition Metal
Substituted MnP. II. Mn\textsubscript{1−t}V\textsubscript{t}P (0.00 ≤ t ≤ 0.25)

HELMER FJELLVÅG and ARNE KJEKSHUS

Kjemisk Institutt, Universitetet i Oslo, Blindern, N-0315 Oslo 3, Norway

Mn\textsubscript{1−t}V\textsubscript{t}P is studied for 0.00 ≤ t ≤ 0.25 by X-ray and neutron diffraction below and above room temperature. Magnetic susceptibility data for the same samples are also included. The MnP type atomic arrangement prevails under these conditions in para-, ferro- or helimagnetic states. The results are discussed in relation to other information on Mn\textsubscript{1−t}V\textsubscript{t}P and related phases.

The current interest in the Mn\textsubscript{1−t}T\textsubscript{t}P (T=transition metal) and MnP\textsubscript{1−x}X\textsubscript{x} (X=metalloid) phases originates from the rather unique magnetic properties of MnP (cf. Ref. 1 and references therein). The solid solution phases have opened for additional opportunities to study more and further details of the properties of MnP. In addition, the properties of Mn\textsubscript{1−t}T\textsubscript{t}P and MnP\textsubscript{1−x}X\textsubscript{x} are interesting in their own right.

The structural and magnetic properties of Mn\textsubscript{1−t}Co\textsubscript{t}P are considered in the preceeding paper\textsuperscript{2} of this series, and discussed in relation to the properties of MnP itself. The present contribution concerns Mn\textsubscript{1−t}V\textsubscript{t}P, properties of which have also been disclosed in earlier communications.\textsuperscript{3,4}

RESULTS AND DISCUSSION

(i) Atomic arrangement. In conformity with Ref. 3, Mn\textsubscript{1−t}V\textsubscript{t}P with 0.00 ≤ t ≤ 0.25 exhibits the MnP type atomic arrangement (here using \textit{Pnma} setting, c>a>b) at, and below, room temperature. The generally sharp Bragg reflections together with the lack of additional superstructure reflections in the X-ray and neutron diffraction diagrams confirm that Mn and V are randomly (long range) distributed over the metal sub-lattice. The unit cell dimensions and positional parameters, as derived from powder neutron diffraction data, are listed in Table 1.

The unit cell dimensions of Mn\textsubscript{1−t}V\textsubscript{t}P versus t (0.00 ≤ t ≤ 0.25) at 10 and 293 K in Fig. 1 go well together with the corresponding room temperature data in Ref. 3. The slightly larger scatter of the neutron (compared with the X-ray) diffraction points in Fig. 1 originates from the methodology of the former technique. As pointed out in Refs. 2, 5, an expansion of the b axis with decreasing temperature can be used as an indicator of ferro- (F) and/or helimagnetic (H\textsubscript{c}) states. The reversal of b between 293 and 10 K for 0.00 ≤ t ≤ 0.20 in Fig. 1 thus concurs with the fact that this is just the domain of the F and H\textsubscript{c} phases of Mn\textsubscript{1−t}V\textsubscript{t}P [see (iii) and Ref. 4].

The thermal expansion curves for t=0.05, 0.10 and 0.20 (Fig. 2) also contain some indications of
Table 1. Unit cell dimensions and positional parameters with standard deviations for Mn$_{1-x}$V$_x$P as derived by Rietveld analysis of powder neutron diffraction data. Space group Pnma; Mn/V in 4c and P in 4c. (Nuclear $R_n$-factors ranging between 0.03 and 0.07; magnetic $R_m$-factors ranging between 0.03 and 0.08; profile $R_p$-factors ranging between 0.08 and 0.13; 20–25 nuclear reflections.)

<table>
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<tr>
<th>$t$</th>
<th>T (K)</th>
<th>$a$ (pm)</th>
<th>$b$ (pm)</th>
<th>$c$ (pm)</th>
<th>$x_T$</th>
<th>$z_T$</th>
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<td>0.1848(13)</td>
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Fig. 2. Unit cell dimensions versus temperature (T<300 K) for (a) \(\text{Mn}_{0.95}\text{V}_{0.05}\text{P}\), (b) \(\text{Mn}_{0.90}\text{V}_{0.10}\text{P}\) and (c) \(\text{Mn}_{0.80}\text{V}_{0.20}\text{P}\). Calculated error limits do not exceed the size of symbols. Circles and squares represent results derived from X-ray and neutron diffraction data, respectively. \((1\ \text{Å}=10^2\ \text{pm})\) \(T_C\), \(T_N\) and \(T_S\) refer to the \(P \leftrightarrow F\), \(P \leftrightarrow H_c\) and \(F \leftrightarrow H_e\) transition temperatures, respectively, given in (iii).
Fig. 3. Interatomic distances \((T-T, \text{ average } T-P)\) at 10 and 293 K as functions of \(t\) in \(\text{Mn}_{1-x}\text{V}_x\text{P}\). \(T\) denotes here average Mn, V. Indices \(i,j\) on the \(T-T\) distances \((d_{ij})\) refer to the numbering of \(T\) given in Ref. 5. Error bars are derived from the calculated, maximum standard deviations. Concerning the curves see the text.

deviations for \(0.00 \leq t \leq 0.25\) and \(10 \leq T \leq 293\) K. This result concurs with the findings for other \(\text{Mn}_{1-x}\text{V}_x\text{P}\) phases\(^2,8\) and the geometrical considerations in Refs. 9, 10 (taking into account that \(\text{Mn}_{1-x}\text{V}_x\text{P}\) with \(0.00 \leq t \leq -0.75\) probably retains the MnP type structure up to the melting point).

The compositional variations at 10 and 293 K of the average metal–phosphorous and the three shortest metal–metal interatomic distances in \(\text{Mn}_{1-x}\text{V}_x\text{P}\) (as derived from the data in Table 1) are shown in Fig. 3. As seen from the error bars shown on the illustration, the second shortest metal–metal distance \((d_{21})\) which corresponds to zig-zag chains along the \(b\) direction is particularly hampered by the inaccuracies in the positional parameters. On the other hand, the third shortest metal–metal distance \((d_{11})\) equals the \(b\) axis and is accordingly very precisely determined. On the basis of the experimental points and error bars in Fig. 3 only \(d_{11}\) is subject to a significant change between 10 and 293 K. However, the clear-cut trend for the average metal–phosphorous distance suggests that also this quantity is temperature dependent. Smaller temperature and concentration variations can easily be masked by the scatter of the positional parameters within their appreciable standard deviations. Since the positional parameters show indications of invariability with respect to \(T\) and \(t\), their averages were combined with the observed unit cell dimensions (Table 1) to generate interatomic distances on this basis. The resulting curves in Fig. 3 show that this procedure (as expected) closely simulates the points, thus emphasizing the correlation to unit cell dimensions in such cases. We intend to return to this aspect in a broader context.

(ii) Magnetic susceptibility. The reciprocal magnetic susceptibility \(\text{versus}\) temperature characteristics for \(\text{Mn}_{1-x}\text{V}_x\text{P}\) with \(0.00 \leq t \leq 0.30\) in Ref. 3 differ from those for other, corresponding-

Fig. 4. Inverse magnetic susceptibility as function of temperature for \(\text{Mn}_{1-x}\text{V}_x\text{P}\) with \(t=0.05, 0.10, 0.15, 0.20\) and 0.25.

ly diluted Mn$_{1-t}$P phases by their non-linear (slightly sigmoidal) shape. Hence, the $\chi^{-1}$ (T) curves for the present neutron diffraction samples were recorded, and the results in Fig. 4 show that also Mn$_{1-V}$P indeed falls nicely into the general pattern. Since, renewed measurements on the samples used in Ref. 3 confirm the earlier findings, there had to be a distinction between the two sets of samples. Even very careful examination by the X-ray (Guinier) diffraction technique failed to bring out any such distinction. However, analyses of a few samples by Auger and/or ESCA show clear-cut evidence of surface oxidation. The surface oxidation appears indeed to be more severe for the samples of Ref. 3 than for the present samples, but we were unfortunately unable to pursue the problem further.

The $\chi^{-1}$ (T) curves for Mn$_{1-V}$P (Fig. 4; see Ref. 3 for $t \gg 0.40$, the magnetic consequences of the oxidation being evidently less important for V rich samples) show a gradual change in character. The straight lines for low substitution levels of V, convert to curves which are concave towards the temperature axis when the V content increases. This trend concurs with the findings for all Mn$_{1-t}$P phases which we have examined.

The $\chi^{-1}$ (T) curves for $t=0.05$, 0.10 and 0.15 fulfil Curie-Weiss law $[\chi^{-1}=C^{-1}(T-\theta)]$ for the entire temperature interval shown in Fig. 4 whereas those for $t=0.20$ and 0.25 can be approximated by two such relationships. The paramagnetic moment ($\mu_{\text{eff}}=[8C_{\text{mol}}]^{1/2}$) and Weiss constant ($\theta$) as derived from the Curie-Weiss regions are listed in Table 2, which also includes the number of unpaired spins (2S) according to the “spin only” approximation ($\mu_{\text{eff}}=g[5(S+1)]^{1/2}$ with $g=2$). The data for the “low” temperature Curie-Weiss regions reveal a decline in $\theta$, $\mu_{\text{eff}}$ and 2S, whereas the “high” temperature regions lead to appreciably lower values for $\theta$ and roughly concentration independent $\mu_{\text{eff}}$ and 2S. However, judging from the general trend in the shape of the $\chi^{-1}$ (T) curves of Mn$_{1-t}$P it seems likely that parameters derived from the “high temperature Curie-Weiss regions” have no physical significance. This problem will in any case be left open in this context.

The $\theta$ values for Mn$_{1-V}$P with $t=0.05$ and 0.10 concur with the Curie temperatures ($T_C$) derived by neutron diffraction and/or magnetization measurements, whereas those for $t=0.15$ and 0.20 fall above the Néel temperatures ($T_N$) determined by neutron diffraction [see (iii) and Ref. 4]. These findings are as expected since $T_C$ and $\theta$ normally agree within some 20 K as opposed to $T_N$ and $\theta$ which may differ appreciably depending on the number and kinds of magnetic exchange interactions involved. The MnP, Hf type magnetic structure is indeed governed by several different exchange interactions (cf., e.g., Refs. 12, 13). The relation between 2S and the magnetic moments deduced by neutron diffraction and magnetization measurements [see (iii) and Ref. 4] is shown in Fig. 5. As seen from the illustration there is an almost perfect match between the extrapolated magnetization moments and the helimagnetic moments ($\mu_{\text{hel}}$). In line with the findings for all Mn$_{1-t}$P (and other phases the paramagnetic 2S values are considerably higher than the ordered moments $\mu$, but both curves in Fig. 5 show a decrease with increasing $t$. These aspects will be discussed in relation to the corresponding data for all Mn$_{1-t}$P phases.

(iii) Magnetic structures. The magnetic phase diagram for Mn$_{1-V}$P for 0.00$\leq t \leq 0.50$ and 0$<T<300$ K in Ref. 4 comprises in addition to the P, F and H$_2$ phases a spin glass (SG) region for $\sim 0.30 < t < \sim 0.50$. The present data were taken into account when the diagram was prepared.

By the neutron diffraction technique, the occurrence of the F phase could only be unequivocally established for $t=0.05$, $T_C=260\pm 5$ K, $\mu_r=0.8 \mu_B$ (direction of moments parallel to $b$) at 160 K. The neutron diffraction diagrams for $t=0.10$ between 200 and 160 K also gave indications of the F phase, but the narrow existence

<table>
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<tr>
<th>$t$</th>
<th>$\theta$ (K)</th>
<th>$\mu_{\text{eff}}$ (\mu_B per T)</th>
<th>2S (per T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>265$\pm 10$</td>
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<td>1.77$\pm 0.08$</td>
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<tr>
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<td>250$\pm 10$</td>
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<td>1.75$\pm 0.08$</td>
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<tr>
<td>0.15</td>
<td>185$\pm 10$</td>
<td>2.51$\pm 0.10$</td>
<td>1.70$\pm 0.08$</td>
</tr>
<tr>
<td>0.20$^a$</td>
<td>160$\pm 15$</td>
<td>2.38$\pm 0.15$</td>
<td>1.58$\pm 0.12$</td>
</tr>
<tr>
<td>0.20$^b$</td>
<td>85$\pm 15$</td>
<td>2.59$\pm 0.15$</td>
<td>1.77$\pm 0.12$</td>
</tr>
<tr>
<td>0.25$^a$</td>
<td>135$\pm 15$</td>
<td>2.27$\pm 0.15$</td>
<td>1.48$\pm 0.12$</td>
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<tr>
<td>0.25$^b$</td>
<td>55$\pm 15$</td>
<td>2.48$\pm 0.15$</td>
<td>1.67$\pm 0.12$</td>
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$^a$ For $T<\sim 450$ K. $^b$ For $T>\sim 450$ K.
range from $T_C=216\pm5$ K to $T_S=152\pm5$ K and $\mu_F<0.5\mu_B$ at 160 K prevents a more precise evaluation. No sign of the F phase was observed for $t=0.15, 0.20$ and 0.25.

The F to H$_C$ phase transition is established for $t=0.05$ and 0.10, numerical values for $T_S$ being given in Table 3. Although this transition is likely to be of first order (cf. Refs. 1, 2) no indication of hysteresis was observed in the temperature variation of the integrated intensity of the 000$^\pm$ satellite for $t=0.05$ and 0.10 (Fig. 6). As is the case for all Mn$_{1-t}$V$_t$P phases which we have studied$^{2,8}$ the temperature characteristics of the integrated intensity ($I$) of 000$^\pm$ are rather broad. This applies also to the curves for $t=0.15$ and 0.20 in Fig. 6 which refer to the H$_C$ $\Leftrightarrow$ P transition ($T_N$ is listed in Table 3). The origin of the maxima in $I$ versus T for $t=0.05$ and 0.10 is not uncovered. A simple explanation would be that this behaviour reflects a temperature variation of the phase angle between the spirals. However, there are also other, and perhaps more likely, possibilities which cannot be tested before, say, single crystal

<table>
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<tr>
<th>$t$</th>
<th>$\tau$/$2\pi c^*$</th>
<th>$\mu_H$ ($\mu_B$)</th>
<th>$\phi_{1,2}$ ($^\circ$)</th>
<th>$T_S$ (K)</th>
<th>$T_N$ (K)</th>
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* $R_{spiral}$ ranging between 0.04 and 0.08; 8–12 magnetic satellite reflections.
data come to hand. It may finally be appropriate to recapitulate from Ref. 4 that the $H_c$, $F$ and $P$ phases in the phase diagram of Mn$_{1-x}$V$_x$P very likely meet in a triple point.

The original and simplest model for the magnetic structure of the $H_c$ phase of MnP was adopted for Mn$_{1-x}$V$_x$P. Numerical values for the variable parameters of the model (viz. the propagation vector $\tau_c$ of the spirals, the helimagnetic moment $\mu_H$ and the phase angle $\phi_{1,2}$ between the spirals through atoms 1 and 2, cf. Ref. 2) are listed in Table 3. The corresponding results for a powder sample of MnP are included in Table 3 for comparison (cf. also the discussion in Ref. 2).

The compositional variations of $\tau_c$, $\mu_H$ and $\phi_{1,2}$ at 10 K are evident from Table 3 (cf. also Ref. 4). In order to determine the temperature variations of the parameters for a given $t$ the positions and intensities of the satellites were examined at various temperatures. The $\tau_c$ versus temperature relationships (easily and accurately established) for $t=0.00$, 0.05, 0.10, 0.15 and 0.20 are shown in Fig. 7. As seen from the illustration $\tau_c$ undergoes a smooth, continuous variation with $T$, and the possibility of “lock-in” effects at integer numbers in the periodicity (viz. at $|\tau_c|^{-1}$ corresponding to 6, 7, 8 and 9 $c$ edge lengths) can apparently be ruled out. Less decisive information is obtained for the temperature changes in $\mu_H$ and $\phi_{1,2}$. For $t=0.10$ (with $T_S=152\pm5$ K and $T_C=216\pm5$ K$^4$) $\mu_H=0.8\pm0.1$ $\mu_B$ and $\phi_{1,2}=33\pm8^\circ$ at 130 K. For $t=0.15$ and 0.20 (which do not undergo the $H_c$ to F transition; cf. Ref. 4) $\mu_H$ is clearly continuously reduced to zero at $T_N$ whereas $\phi_{1,2}$ appears to be maintained essentially unchanged from 10 K to $T_N$. (Approximate estimates for $\mu_H$ and $\phi_{1,2}$ could only be obtained at temperatures where $\mu_H$ remains approximately constant.)

No indication of any kind of co-operative magnetism has been obtained for $t=0.25$. In line with the findings in Ref. 4 we suggest that the SG region of the Mn$_{1-x}$V$_x$P phase extends to $t=0.25$ (where the freezing temperature should be some 40 K). The border between the $H_c$ and SG regions should accordingly be narrowed to 0.20$<t<0.25$. A discussion of the SG regions in Mn$_{1-x}$V$_x$P and Mn$_{1-x}$Co$_x$P appears to require data over and above those available at the present time.

Acknowledgement. This work has received financial support from the Norwegian Research Council for Science and the Humanities.

![Fig. 7. Temperature dependences of the propagation vector ($\tau_c$) for Mn$_{1-x}$V$_x$P with $t=0.00$, 0.05, 0.10, 0.15 and 0.20. Experimental points are only shown for $t=0.15$.](image)

REFERENCES


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