

# On the Structural and Magnetic Properties of $\text{Cr}_{1-t}\text{V}_t\text{P}$ , $\text{Mn}_{1-t}\text{V}_t\text{P}$ and $\text{Mn}_{1-t}\text{Cr}_t\text{P}$

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The pseudo-binary  $\text{CrP-VP}$ ,  $\text{MnP-VP}$ , and  $\text{MnP-CrP}$  systems have been investigated by X-ray diffraction and magnetic susceptibility measurements. The systems containing VP show limited solid solubility, whereas complete solid solubility is found for  $\text{Mn}_{1-t}\text{Cr}_t\text{P}$ . The structures of the ternary, random solid solution phases are of the MnP type except for samples rich in VP, for which the NiAs type prevails. The paramagnetic susceptibilities follow the Curie-Weiss Law only for  $\text{Mn}_{1-t}\text{Cr}_t\text{P}$  ( $t \leq 0.4$ ).

We continue our series of papers on binary and pseudo-binary phases with the MnP type structure by presenting some phase-analytical, structural, and magnetic susceptibility data for  $\text{Cr}_{1-t}\text{V}_t\text{P}$ ,  $\text{Mn}_{1-t}\text{V}_t\text{P}$ , and  $\text{Mn}_{1-t}\text{Cr}_t\text{P}$ . CrP and MnP are known<sup>1-4</sup> to crystallize with the MnP type structure, whereas VP takes<sup>3,5</sup> the NiAs type atomic arrangement. A neutron diffraction study of the cooperative magnetic properties of pseudo-binary MnP type phosphides is in progress.

## EXPERIMENTAL

Samples were made from 99.5% V (A.D. Mackay), 99.99% crushed Mn flakes (Johnson, Matthey & Co.), 99.999% crushed Cr flakes and red P (Koch-Light Laboratories). Binary samples of VP, CrP, and MnP were prepared as described in Refs. 5, 2, and 4, respectively. Ternary samples were made from the binary compounds by a first heat treatment at 1000 °C for 3–4 d, followed by 2–5 further heat treatments at 850–1100 °C for 1 h–1 week, and finally slow cooling or quenching to room temperature. The experimental details concerning X-ray diffraction and magnetic susceptibility measurements have been reported earlier.<sup>5</sup>

## RESULTS

(i) *Homogeneity ranges and atomic arrangements.* Isothermal cross-sections, as derived for samples quenched from 600 °C, show (Fig. 1) gaps in the solid solubility for  $\text{Cr}_{1-t}\text{V}_t\text{P}$  ( $0.60 \pm 0.02 < t < 0.95 \pm 0.02$ ) and  $\text{Mn}_{1-t}\text{V}_t\text{P}$  ( $0.70 \pm 0.02 < t < 0.90 \pm 0.02$ ) and complete solid solubility for  $\text{Mn}_{1-t}\text{Cr}_t\text{P}$ . The limits of the solubility ranges have been determined from the variation of the unit cell dimensions with  $t$ , and further confirmed by application of the disappearing phase principle to the X-ray (Guinier) data. Only ternary samples with metal/non-metal atomic ratios equal to 1.00 have been examined.

Fig. 1 shows that the NiAs type structure prevails at room temperature for  $\text{Cr}_{1-t}\text{V}_t\text{P}$  and  $\text{Mn}_{1-t}\text{V}_t\text{P}$  when  $0.95 \leq t$ , whereas the MnP type is stable for the rest of their homogeneity ranges as well as for  $\text{Mn}_{1-t}\text{Cr}_t\text{P}$ . The two kinds of metal atoms are randomly distributed over the metal sub-lattices in the two types of atomic arrangements. From the variations in unit cell dimensions with  $t$  (Fig. 1b) it may be suggested that complete miscibility in the MnP type region can be obtained for  $\text{Mn}_{1-t}\text{V}_t\text{P}$  at suitable experimental conditions.

In analogy with the findings for the corresponding arsenides,<sup>3,6-11</sup> a second or higher order MnP $\rightleftharpoons$ NiAs type transition may be expected for V rich samples of  $\text{Cr}_{1-t}\text{V}_t\text{P}$  and  $\text{Mn}_{1-t}\text{V}_t\text{P}$ . However, high temperature X-ray diffraction measurements show that this does not occur for  $\text{Mn}_{1-t}\text{V}_t\text{P}$  (Fig. 2).

(ii) *Magnetic susceptibility.* The temperature characteristics of the reciprocal magnetic susceptibility show systematic variation with the composition parameter  $t$  for  $\text{Cr}_{1-t}\text{V}_t\text{P}$ ,  $\text{Mn}_{1-t}\text{V}_t\text{P}$ , and  $\text{Mn}_{1-t}\text{Cr}_t\text{P}$  (Fig. 3). No signs of ferri- or ferromagnetic impurities were found. Apart from

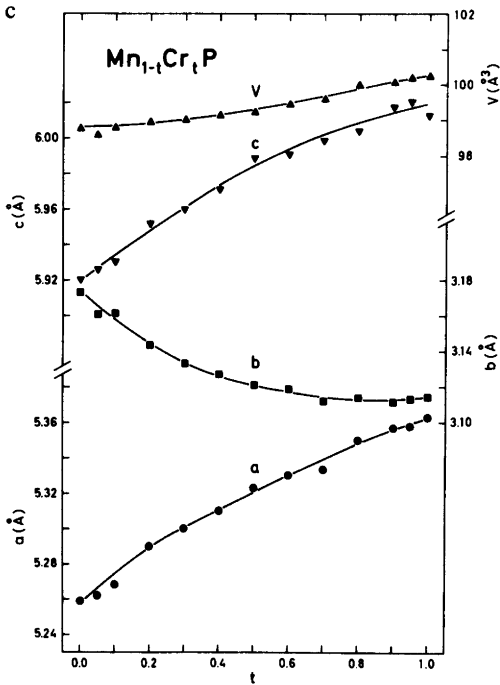
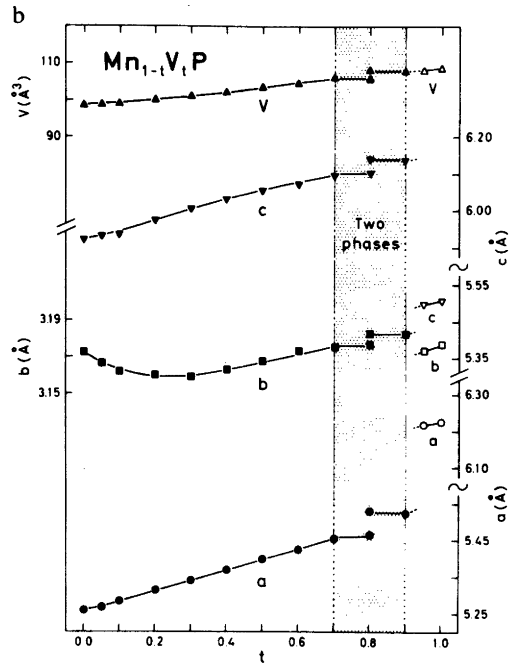
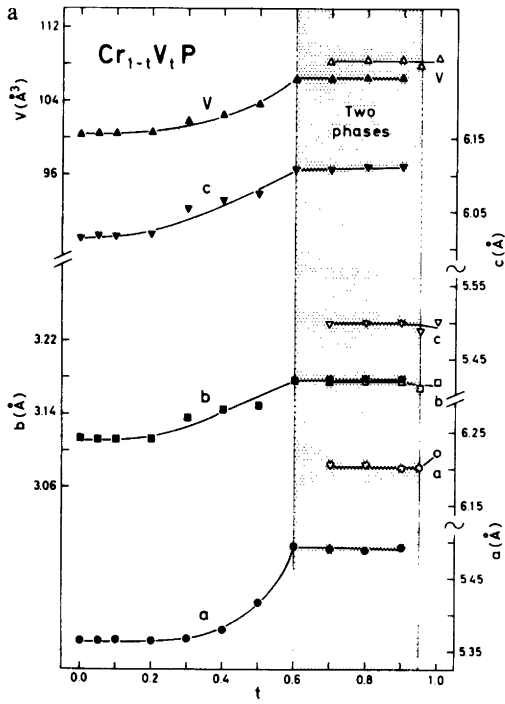


Fig. 1. Room temperature unit cell dimensions of (a)  $\text{Cr}_{1-t}\text{V}_t\text{P}$ , (b)  $\text{Mn}_{1-t}\text{V}_t\text{P}$ , and (c)  $\text{Mn}_{1-t}\text{Cr}_t\text{P}$  as functions of  $t$ . Open and filled symbols refer to NiAs and MnP type structures, respectively, both described in terms of space group  $Pnma$ .

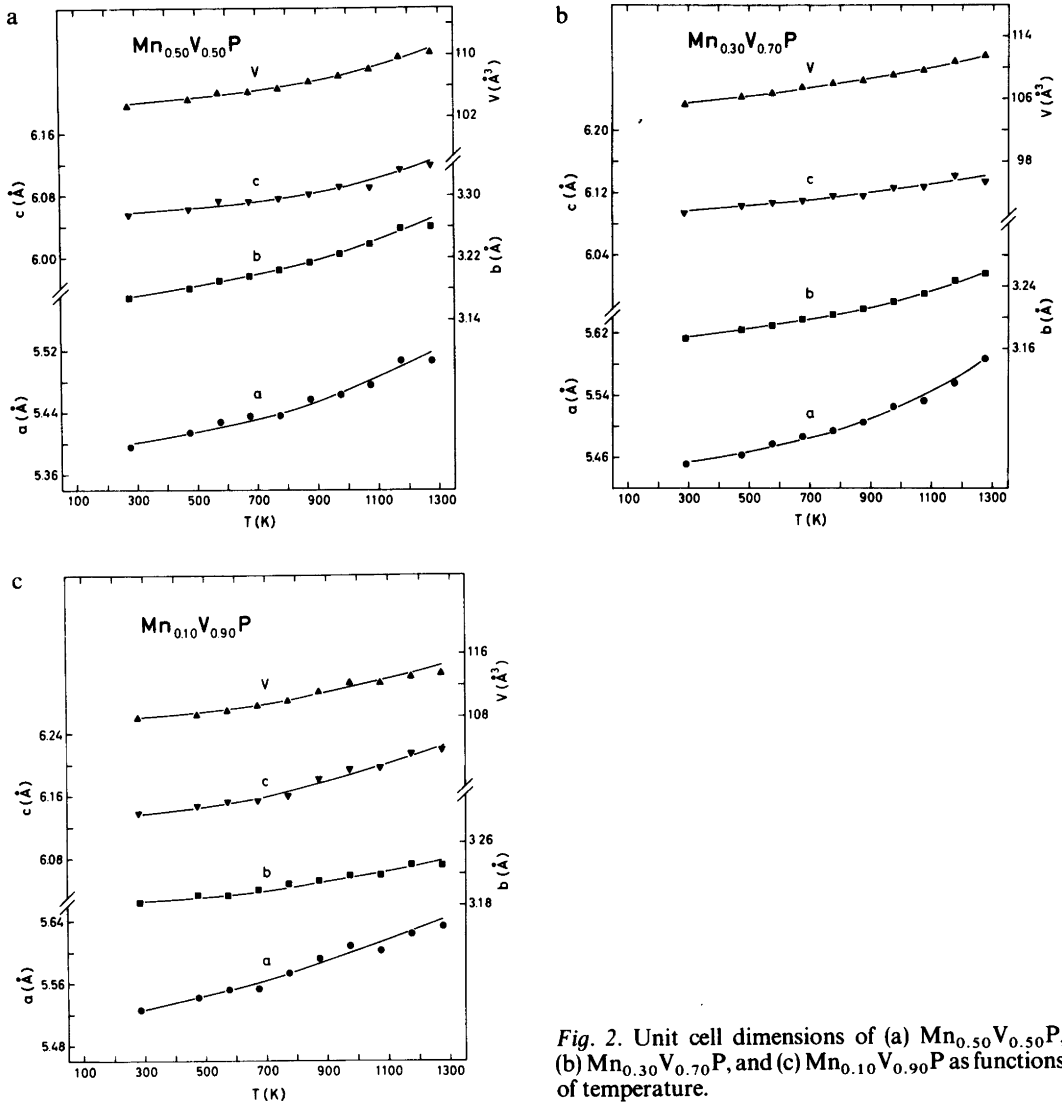


Fig. 2. Unit cell dimensions of (a) Mn<sub>0.50</sub>V<sub>0.50</sub>P, (b) Mn<sub>0.30</sub>V<sub>0.70</sub>P, and (c) Mn<sub>0.10</sub>V<sub>0.90</sub>P as functions of temperature.

Mn<sub>1-t</sub>Cr<sub>t</sub>P for  $t \leq 0.4$  the  $\chi^{-1}(T)$  curves for the ternary samples are generally non-linear. The linear  $\chi^{-1}(T)$  curves for Mn<sub>1-t</sub>Cr<sub>t</sub>P,  $0 \leq t \leq 0.4$ , show that the Curie-Weiss Law is satisfied, values for the Curie constant ( $\theta$ ), paramagnetic moment ( $\mu_p$ ) and number of unpaired electrons ( $2S$ ; "spin only" approximation) being listed in Table 1. These data show that  $\mu_p$ , and thus  $2S$ , stay approximately constant, whereas a gradual reduction in  $\theta$  takes place when the Mn content of the samples decreases.

Table 1. Curie constant, paramagnetic moment, and number of unpaired electrons for Mn<sub>1-t</sub>Cr<sub>t</sub>P samples which fulfil Curie-Weiss Law.

$t$	$\theta(K)$	$\mu_p(\mu_B)$	$2S$
0.00	$340 \pm 10$	$2.9_7 \pm 0.1$	$2.1_4$
0.05	$310 \pm 10$	$2.9_4 \pm 0.1$	$2.1_0$
0.10	$286 \pm 10$	$2.9_9 \pm 0.1$	$2.1_6$
0.20	$253 \pm 10$	$2.9_3 \pm 0.1$	$2.1_0$
0.30	$190 \pm 10$	$2.9_6 \pm 0.1$	$2.1_2$
0.40	$140 \pm 10$	$2.8_9 \pm 0.1$	$2.0_6$

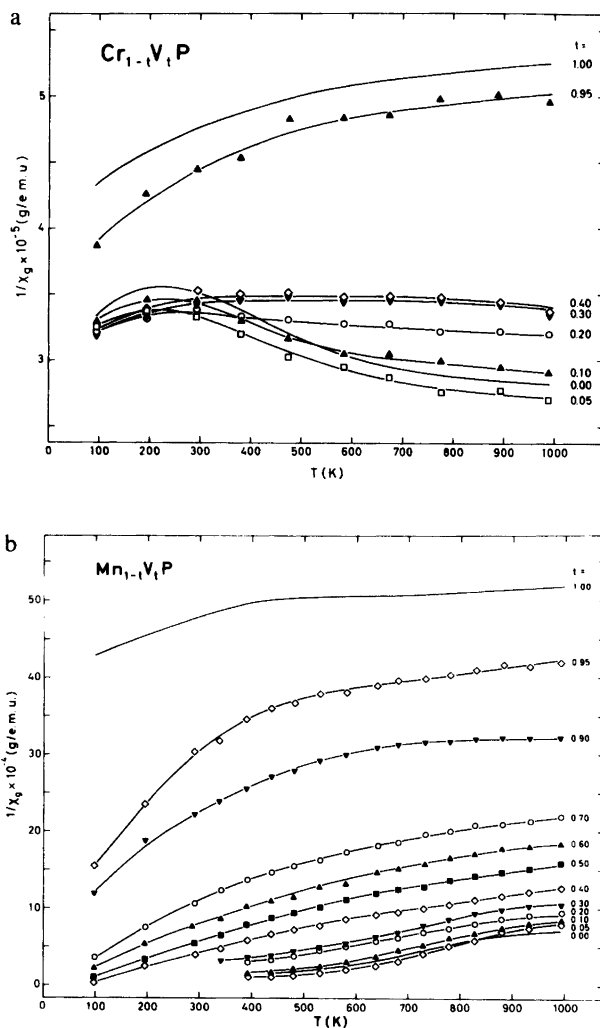


Fig. 3. Reciprocal magnetic susceptibility versus temperature for (a)  $\text{Cr}_{1-t}\text{V}_t\text{P}$  and (b)  $\text{Mn}_{1-t}\text{V}_t\text{P}$ .

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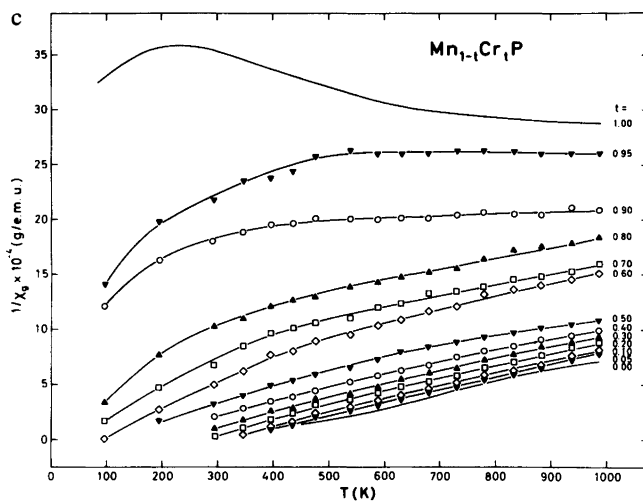


Fig. 3. (c)  $\text{Mn}_{1-t}\text{Cr}_t\text{P}$ .

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