

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

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The pseudo-binary CrP – FeP , MnP – CoP , and FeP – CoP systems have been investigated by X-ray diffraction and magnetic susceptibility measurements. The three systems show complete solid solu-

bility with MnP type structure and random distribution of the metal atoms. The paramagnetic susceptibilities follow the Curie-Weiss Law only for samples rich in MnP .

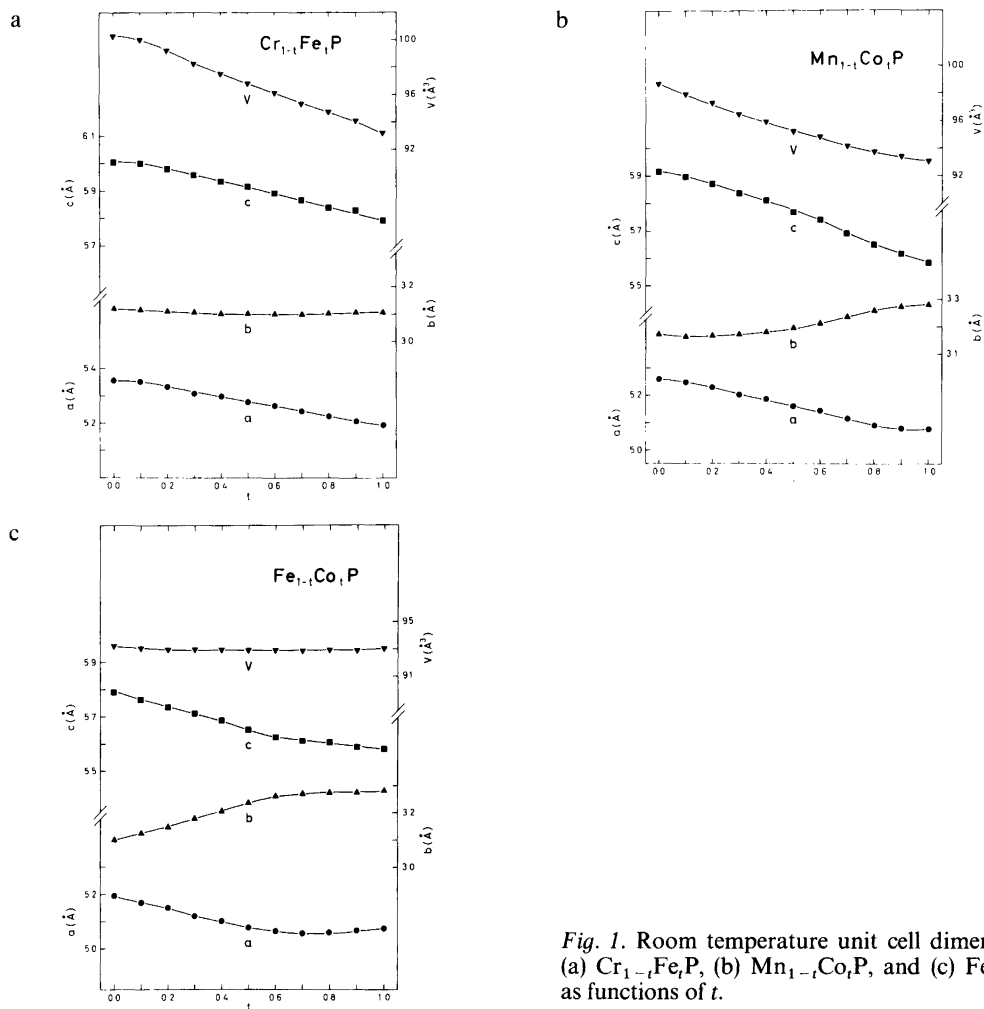


Fig. 1. Room temperature unit cell dimensions of (a) $\text{Cr}_{1-t}\text{Fe}_t\text{P}$, (b) $\text{Mn}_{1-t}\text{Co}_t\text{P}$, and (c) $\text{Fe}_{1-t}\text{Co}_t\text{P}$ as functions of t .

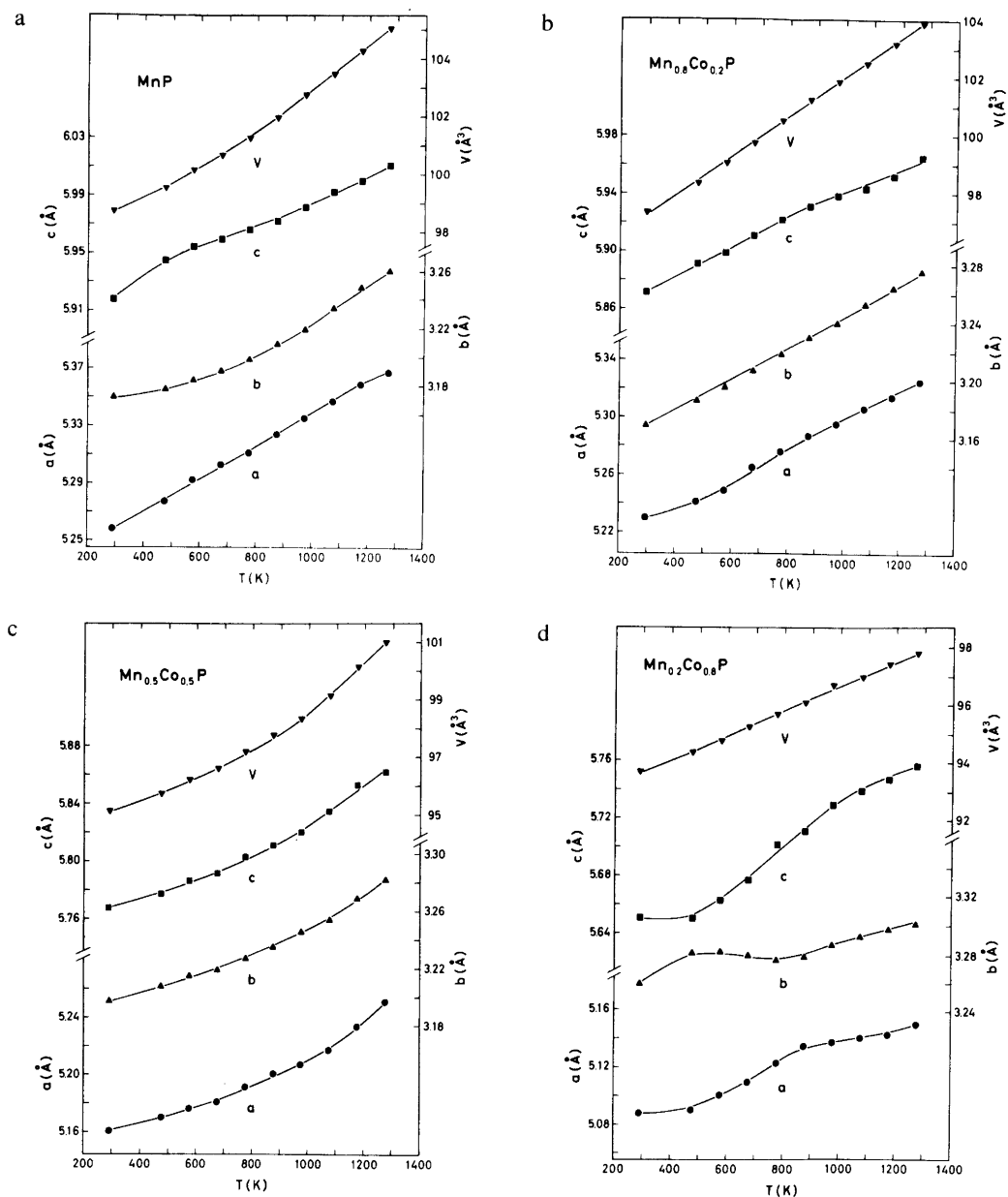
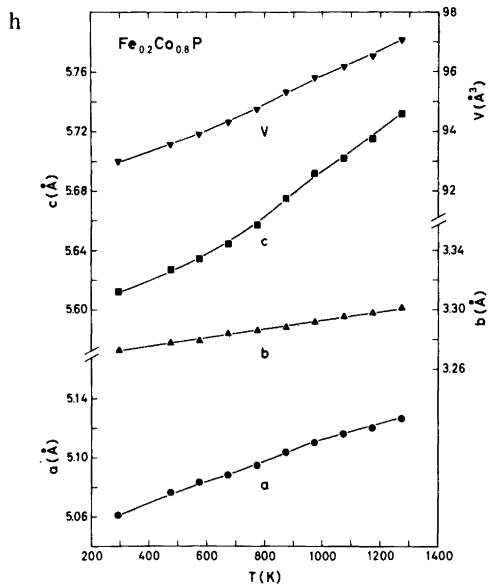
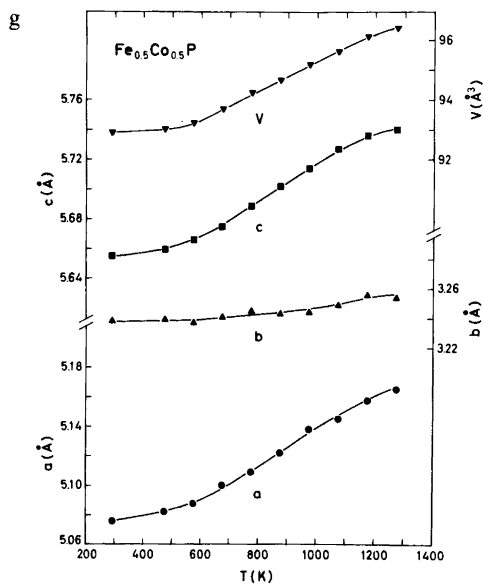
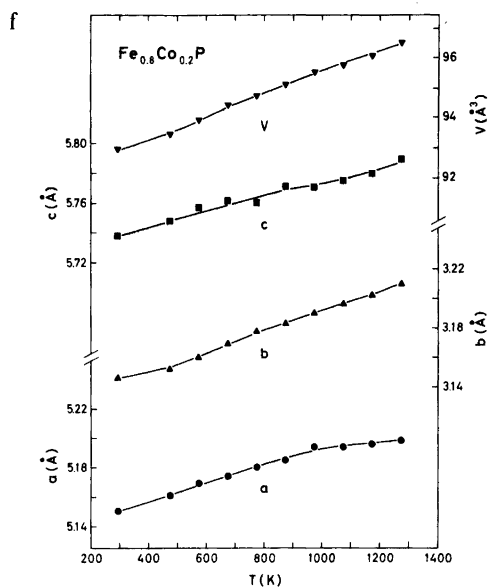
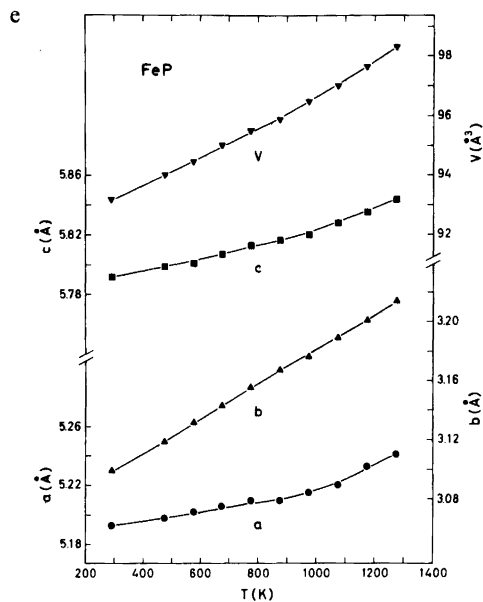


Fig. 2. Unit cell dimensions of (a) MnP, (b) Mn_{0.8}Co_{0.2}P, (c) Mn_{0.5}Co_{0.5}P, (d) Mn_{0.2}Co_{0.8}P, (e) FeP,

The mono-phosphides and -arsenides of the transition metals Cr, Mn, Fe, and Co take the MnP type structure. The structural and magnetic properties of the mono-arsenides (both binary and pseudo-binary) have been extensively studied at this Institute

and are now well characterized. The corresponding properties of the mono-phosphides have been given less attention. The behaviour of the binary compounds is mainly disclosed,¹⁻¹³ whereas only a few characteristics have been reported for the pseudo-



(f) Fe_{0.8}Co_{0.2}P, (g) Fe_{0.5}Co_{0.5}P, and (h) Fe_{0.2}Co_{0.8}P as functions of temperature.

binary mono-phosphides.¹⁴⁻¹⁸ As a continuation of our programme on MnP type phases, attention has now been focussed on these ternary phosphides.

EXPERIMENTAL

Samples were made from 99.99% Mn and Fe, 99.99+ % Co (Johnson, Matthey & Co.; crushed Mn flakes, turnings from rods of Fe and Co), 99.999% crushed Cr flakes and red P (Koch-Light

Laboratories). Binary samples of FeP and CrP were prepared as described in Refs. 10 and 11. CoP was obtained after two heat treatments, one at 1000 °C for 2 d, followed by 1 d at 1200 °C and 2 d at 1000 °C. MnP was prepared by a first heat treatment at 650 °C for 1 week, the second at 1100 °C for 1 h followed by slow cooling to 600 °C. Ternary samples were made from the binary compounds by one heat treatment at 1000 °C for 2 d followed by another of 1 d at 1000 °C, 1 week at 850 °C, slow cooling to

600 °C and then quenching. The experimental details concerning X-ray diffraction and magnetic susceptibility measurements have been reported earlier.¹⁹

RESULTS

(i) *Homogeneity ranges and atomic arrangement.* Isothermal cross-sections of $\text{Cr}_{1-t}\text{Fe}_t\text{P}$, $\text{Mn}_{1-t}\text{Co}_t\text{P}$, and $\text{Fe}_{1-t}\text{Co}_t\text{P}$, as derived for samples quenched from 600 °C, show (Fig. 1) that these systems exhibit complete solid solubility. Only ternary samples with metal/non-metal atomic ratios equal to 1.00 have

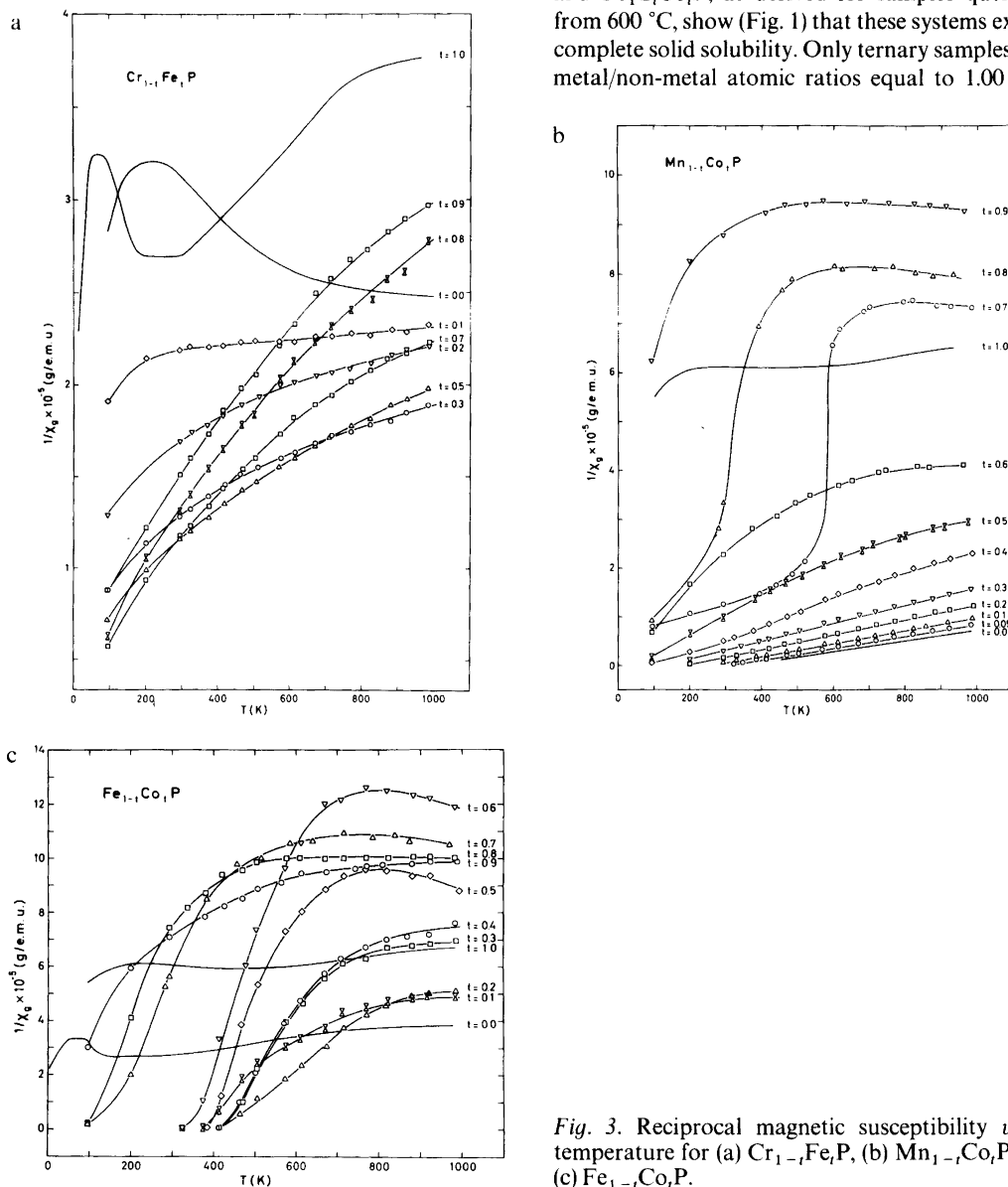


Fig. 3. Reciprocal magnetic susceptibility versus temperature for (a) $\text{Cr}_{1-t}\text{Fe}_t\text{P}$, (b) $\text{Mn}_{1-t}\text{Co}_t\text{P}$, and (c) $\text{Fe}_{1-t}\text{Co}_t\text{P}$.

Table 1. Curie constant (θ), paramagnetic moment ($\mu_p = \sqrt{8C_M}$), and number of unpaired electrons ($n = 2S_T$) for Mn_{1-t}Co_tP samples which fulfil Curie-Weiss Law.

t	θ (K)	μ_p (μ_B)	$2S_T$
0.00	310 ± 10	2.6 ± 0.1	1.8 ± 0.1
0.05	300 ± 10	2.4 ± 0.1	1.6 ± 0.1
0.10	255 ± 10	2.2 ± 0.1	1.5 ± 0.1
0.20	190 ± 10	2.1 ± 0.1	1.3 ± 0.1
0.30	130 ± 15	1.9 ± 0.1	1.2 ± 0.1
0.40	80 ± 20	1.7 ± 0.1	1.0 ± 0.1

been examined. The diffraction data show that Cr_{1-t}Fe_tP, Mn_{1-t}Co_tP, and Fe_{1-t}Co_tP ($0 \leq t \leq 1$) take the orthorhombic MnP type structure with random distribution of the two kinds of metal atoms. This applies also to samples of approximate composition Mn_{0.2}Co_{0.8}P and Fe_{0.4}Co_{0.6}P for which the axial ratio c/b is $\sqrt{3}$ and hexagonal symmetry (e.g., NiAs type structure) could have been a possibility. This confirms the findings of Rundqvist.¹⁴

A second or higher order transition to the NiAs type structure has been detected above room temperature for many binary and ternary MnP type arsenide phases.^{20,21} However, the high temperature, X-ray diffraction measurements on Mn_{1-t}Co_tP and Fe_{1-t}Co_tP samples with $t=0, 0.2, 0.5$, and 0.8 (results for CrP and CoP being presented earlier²⁰) show no such transition, as demonstrated by the results given in Fig. 2.

(ii) *Magnetic susceptibility.* The temperature characteristics of the reciprocal magnetic susceptibility show systematic variation with the composition parameter t for Cr_{1-t}Fe_tP, Mn_{1-t}Co_tP, and Fe_{1-t}Co_tP (Fig. 3). No signs of ferri- or ferromagnetic impurities were found. The $\chi^{-1}(T)$ curves for Cr_{1-t}Fe_tP and Fe_{1-t}Co_tP are generally non-linear and convex towards the temperature axis. The same applies to Mn_{1-t}Co_tP for $t > 0.4$. $\chi^{-1}(T)$ is, on the other hand, linear to a very good approximation for $0 \leq t \leq 0.4$. The Curie-Weiss Law is accordingly fulfilled, and values for the Curie constant, paramagnetic moment, and number of unpaired electrons according to the "spin only" approximation are listed in Table 1. With decreasing content of Mn there is a gradual reduction in these magnetic parameters. The present findings for Mn_{1-t}Co_tP concur with those of Huber and Ridgley¹ for the paramagnetic state of MnP, and are also reasonably consistent with data (cf., e.g., Refs. 1 and 4) on its ferromagnetic state. It may be

worth noting that MnP itself and its Mn rich ternary derivatives are the only phases with MnP type structure hitherto that fulfil the Curie-Weiss Law over an appreciable temperature interval.

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REFERENCES

- Huber, E. E. and Ridgley, D. H. *Phys. Rev.* 135 (1964) A1033.
- Rundqvist, S. and Nawapong, P. C. *Acta Chem. Scand.* 19 (1965) 1006.
- Komatsubara, T., Kinoshita, K. and Hirahara, E. *J. Phys. Soc. Jpn.* 20 (1965) 2036.
- Felcher, G. P. *J. Appl. Phys.* 37 (1966) 1056.
- Forsyth, J. B., Pickart, S. J. and Brown, P. J. *Proc. Phys. Soc.* 88 (1966) 333.
- Bellavance, D., Vlasse, M., Morris, B. and Wold, A. J. *Solid State Chem.* 1 (1969) 82.
- Ishikawa, Y., Komatsubara, T. and Hirahara, E. *Phys. Rev. Lett.* 23 (1969) 532.
- Wäppling, R., Häggström, L., Rundqvist, S. and Karlsson, E. *J. Solid State Chem.* 3 (1971) 276.
- Felcher, G. P., Smith, F. A., Bellavance, D. and Wold, A. *Phys. Rev. B* 3 (1971) 3046.
- Selte, K. and Kjekshus, A. *Acta Chem. Scand.* 26 (1972) 1276.
- Selte, K., Kjekshus, A. and Andresen, A. F. *Acta Chem. Scand.* 26 (1972) 4188.
- Selte, K., Hjersing, H., Kjekshus, A., Andresen, A. F. and Fischer, P. *Acta Chem. Scand. A* 29 (1975) 695.
- Westerstrandh, B., Lundgren, L., Gäfvert, U. and Karlsson, B. *Phys. Scr.* 15 (1977) 276.
- Rundqvist, S. *Acta Chem. Scand.* 16 (1962) 287.
- Roger, A. and Fruchart, R. *C.R. Acad. Sci. Ser. C* 264 (1967) 508.
- Bonnerot, J., Fruchart, R. and Roger, A. *Phys. Lett. A* 26 (1968) 536.
- Sénateur, J.-P., Roger, A., Fruchart, R. and Chappert, J. *C.R. Acad. Sci. Ser. C* 269 (1969) 1385.
- Maeda, Y. and Takashima, Y. *J. Inorg. Nucl. Chem.* 35 (1973) 1219.
- Selte, K., Kjekshus, A. and Andresen, A. F. *Acta Chem. Scand.* 26 (1972) 3101.
- Selte, K. and Kjekshus, A. *Acta Chem. Scand.* 27 (1973) 3195.
- Selte, K., Kjekshus, A., Andresen, A. F. and Zięba, A. *J. Phys. Chem. Solids* 38 (1977) 719.

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