Short Communication

Structural and Magnetic Properties of $Mn_{1-t}Fe_tP$ ($0.80 \leqslant t \leqslant 1.00$)

Helmer Fjellvåg,[a] Arne Kjekshus[a]* and Arne F. Andresen[b]

[a]Kjemisk Institutt, Universitetet i Oslo, Blindern, N-0315 Oslo 3, Norway and [b]Institutt for Energiteknikk, N-2007 Kjeller, Norway

The MnP-rich part ($0.00 \leqslant t \leqslant 0.30$) of the ternary solid solution phase $Mn_{1-t}Fe_tP$ exhibits[1] helimagnetism (H_c type) at low temperatures whereas ferromagnetism is established for a more restricted composition ($0.00 \leqslant t \leqslant 0.12$)[1,2] and temperature ($T_S < T < T_C$; S = spiral, C = Curie) interval.

According to magnetic susceptibility measurements,[2] it is feasible that the helimagnetic arrangement is retained throughout the entire solid solution phase,[3] from MnP to FeP. However, the phase angle ($\varphi_{1,2}$) between the spirals in the helimagnetic structure of FeP[4] differs appreciably from that of MnP[1], and the compositional (t) variation of $\varphi_{1,2}$ for $0.00 \leqslant t \leqslant 0.28$ is quite small. It is accordingly an open question as to whether the homogeneity range for the helimagnetic phase extends over the entire composition range of the crystallographic solid solution phase. In an attempt to answer this question, a powder neutron diffraction study of $Mn_{1-t}Fe_tP$ with $0.80 \leqslant t < 1.00$, was carried out.

Experimental

Samples of the binary phases MnP and FeP were synthesized as described in Refs. 1,5. Samples of $Mn_{1-t}Fe_tP$ were made by heating appropriate amounts of mixtures of MnP and FeP in evacuated, sealed silica tubes. Three heating cycles at 1000 °C for 5 d, with intermediate crushings at room temperature, were adopted before slowly cooling (over 1 d) to room temperature. The homogeneity of the samples was checked by powder X-ray diffraction (Guinier technique, $CuK\alpha_1$ radiation, Si as internal standard). Powder neutron diffraction data were collected on the OPUS III

*To whom correspondence should be addressed.

two-axis diffractometer accommodated at the JEEP II reactor, Kjeller, using neutrons of wavelength 187.7 pm. Temperatures between 10 and 293 K were obtained by using a Displex cooling system. The Hewat[6] version of the Rietveld[7] programme was applied in the least squares refinements of the crystal structure parameters. The nuclear scattering lengths $b_{Mn} = -3.7$, $b_{Fe} = 9.5$ and $b_p = 5.1$ fm were taken from Ref. 8.

Results and discussion

The powder X-ray and neutron diffraction patterns of $Mn_{1-t}Fe_tP$ ($0.80 \leqslant t \leqslant 1.00$) are in accordance with an MnP type solid solution phase where the Mn and Fe atoms (note the marked difference in scattering lengths) are long-range distributed at random over the metal sublattice. The unit cell dimensions and positional parameters (in terms of space group $Pnma$, $c > a > b$) derived from the Rietveld refinements of the powder neutron diffraction data are given in Table 1 together with corresponding single crystal X-ray data for FeP quoted from Ref. 9.

The room temperature unit cell dimensions for the solid solution phase in Table 1 agree reasonably well with those found by Bonnerot et al.[3] Only a small contraction of the axes takes place on cooling from 293 to 10 K. The refined positional parameters from the Rietveld analyses agree almost completely with those reported for the binary end phase FeP.[9]

The temperature variations of the magnetic susceptibility of samples with $t = 0.80$ and 0.90 were found to obey the Curie-Weiss law over appreciable temperature intervals (Fig. 1). The present findings for $t = 0.80$ $\mu_{eff} = 2.04 \pm 0.10$ μ_B ($2S = 1.26 \pm 0.10$ calculated from $\mu_{eff} = g[S(S+1)]^{1/2}$ with $g = 2$) and $\theta = -115 \pm 20$ K

Table 1. Unit cell dimensions and positional parameters with standard deviations for $Mn_{1-t}Fe_tP$ derived by Rietveld refinement of powder neutron diffraction data. Space group Pnma; Mn,Fe in 4c and P in 4c. (Nuclear R_n factors ranging between 0.03 and 0.04, profile R_p factors between 0.09 and 0.13; 19–24 nuclear reflections.)

t	T(K)	a(pm)	b(pm)	c(pm)	$x_{Mn,Fe}$	$z_{Mn,Fe}$	x_P	z_P
0.80	293	520.92(4)	311.35(2)	581.73(4)	0.0021(14)	0.1993(7)	0.1924(14)	0.5670(12)
	10	520.30(3)	310.60(2)	581.11(4)	0.0026(11)	0.2002(7)	0.1895(13)	0.5666(11)
0.90	293	520.20(4)	310.82(2)	580.58(4)	0.0029(14)	0.1992(8)	0.1929(17)	0.5669(15)
	100	519.81(3)	309.48(2)	580.10(4)	0.0010(14)	0.1995(7)	0.1912(17)	0.5673(14)
	10	519.69(4)	309.41(2)	580.02(5)	0.0023(15)	0.2001(9)	0.1898(21)	0.5663(16)
1.00[a]	293	519.3(1)	309.9(1)	579.2(1)	0.0020(4)	0.2004(3)	0.1912(7)	0.5684(6)

[a]Quoted from Ref. 9.

concur well with the results of Iwata et al.[10] μ_{eff} = 1.83 ± 0.05 μ_B, $2S$ = 1.08 ± 0.04 and θ = −1000 ± 50 K are reported for FeP in Ref. 9 and, in particular, the difference in θ between t = 1.00 and 0.80 is unexpectedly large. On the whole, quite different magnetic susceptibility properties are reported [9–13] for FeP, and we therefore decided to make an attempt to clarify the origin of the discrepancies.
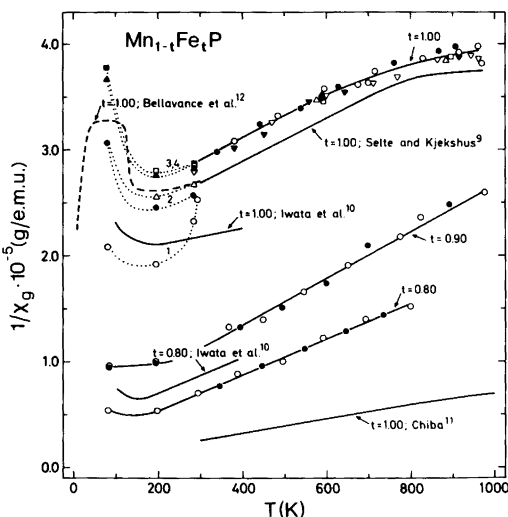

Fig. 1. Inverse magnetic susceptibility versus temperature for FeP, $Mn_{0.10}Fe_{0.90}P$ and $Mn_{0.20}Fe_{0.80}P$. Open and filled symbols represent measurements recorded under increasing and decreasing temperature conditions, respectively. For the curves numbered 1–4 for FeP (T < 300 K), see text. Data from Refs. 9–12 are included for purpose of comparison.

The present magnetic susceptibility measurements were performed on ensembles of small FeP single crystals grown from tin melts. The results obtained for T > 300 K agree quite well with those in Ref. 9 (Fig. 1). For T < 300 K, more complicated features were revealed. The recorded magnetic susceptibility changed systematically on going through repeated cycle series between 80 and 1000 K. After four such cycles (increasing and decreasing temperature runs numbered 1–4 in Fig. 1), approximately the same $\chi^{-1}(T)$ relationship as reported in Refs. 9, 12 was obtained. The findings are believed to reflect an increasing degree of oxidation on the crystal surfaces when the samples are subjected to the measurements at the highest temperatures (say 800–1000 K). A variable degree of partial sample oxidation appears to provide a natural explanation for the appreciable discrepancies in $\chi^{-1}(T)$ for FeP. In accordance with common metallurgical experience, the problem becomes less severe when Mn is introduced as a solid substituent into the Fe sublattice. In order to obtain a perhaps more correct $\chi^{-1}(T)$ curve for FeP, the measurements should be performed on larger single crystal specimens.

FeP takes a double spiral (H_c type[14]) magnetic structure at temperatures below T_N = 125 ± 1 K.[4] The magnetic moments ($\mu_{H,average}$ = 0.41 μ_B) rotate in the ab plane, the propagation vector τ_c = $0.20 \cdot 2\pi c^*$ is parallel to the c axis, while the phase difference between the independent spirals is $\varphi_{1,2}$ = 168.8°.[4] For $Mn_{0.72}Fe_{0.28}P$, the corresponding parameters were found[1] to be T_N = 175 ± 10 K, τ_c = (0.260 ± 0.008)·$2\pi c^*$, μ_H = 0.72 ± 0.14 μ_B and $\varphi_{1,2}$ = 30 ± 20°. For $Mn_{0.10}Fe_{0.90}P$ and

228

$Mn_{0.20}Fe_{0.80}P$, it proved impossible to detect any satellite reflections in the low temperature powder neutron diffraction diagrams. Such reflections may be difficult to observe due to the small magnitude of the ordered moments, but may also be due to severe peak broadening of the satellites as a result of (slight) compositional variation throughout the sample together with an appreciable variation in τ_c with t.

The extension of the H_c type long-range magnetic order of FeP into a ternary region, has hitherto only been observed for $FeP_{1-x}As_x$.[15] In the latter phase, the H_c mode extends up to $x \approx 0.10$, whereas no $000^{\pm}$ satellite reflection (trademark for the H_c mode) could be detected for higher substitution levels. In this way, the findings for $FeP_{1-x}As_x$ resemble those for $Mn_{1-t}Fe_tP$. We believe that the helimagnetic H_c type long-range order in $Mn_{1-t}Fe_tP$ (as well as in $FeP_{1-x}As_x$) is already converted into spin- glass-like properties for a low substitution of Mn for Fe or As for P.

References

1. Fjellvåg, H., Kjekshus, A. and Andresen, A. F. *Acta Chem. Scand. A 38* (1984) 711.
2. Roger, A. and Fruchart, R. *C.R. Acad. Sci. C 264* (1967) 508.
3. Bonnerot, J., Fruchart, R. and Roger, A. *Phys. Lett. A 26* (1968) 536.
4. Felcher, G. P., Smith, F. A., Bellavance, D. and Wold, A. *Phys. Rev. B 3* (1971) 3076.
5. Fjellvåg, H. and Kjekshus, A. *Acta Chem. Scand. A 38* (1984) 563.
6. Hewat, A. W. The Rietveld Computer Program for the Profile Refinement of Neutron Diffraction Powder Patterns Modified for Anisotropic Thermal Vibrations. *UKAERE Harwell Report RRL 73/897* (1973).
7. Rietveld, H. M. *J. Appl. Crystallogr. 2* (1969) 65.
8. Bacon, G. E. In Yelon, W. B., ed., *Neutron Diffraction Newsletter*, Columbia 1977.
9. Selte, K. and Kjekshus, A. *Acta Chem. Scand. 26* (1972) 1276.
10. Iwata, N., Fujii, H. and Okamoto, T. *J. Phys. Soc. Jpn. 46* (1979) 778.
11. Chiba, S. *J. Phys. Soc. Jpn. 15* (1960) 581.
12. Bellavance, D., Vlasse, M., Morris, B. and Wold, A. *J. Solid State Chem. 1* (1969) 82.
13. Westerstrandh, B., Lundgren, L., Gäfvert, U. and Carlsson, B. *Physica Scripta 15* (1977) 276.
14. Fjellvåg, H. and Kjekshus, A. *Acta Chem. Scand. A 38* (1984) 1.
15. Selte, K., Kjekshus, A., Oftedal, T. A. and Andresen, A. F. *Acta Chem. Scand. A 28* (1974) 957.