Magnetic behaviour of $(Fe_{0.995}Cr_{0.005})_2P$

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Abstract. Magnetization and Mössbauer measurements are reported on the hexagonal alloy system $(Fe_{0.995}Cr_{0.005})_2P$. It is ferromagnetically ordered with $T_C = 190$ (± 10) K which is about 25 K lower than that of pure Fe_2P. In the high-temperature region the Curie–Weiss law holds. The paramagnetic Curie temperature is 390 (± 10) K, quite in agreement with that of Fe_2P. Analysis of the Mössbauer spectrum at 9 K suggests that the presence of Cr in second coordination sphere of Fe considerably lowers the internal hyperfine fields at Fe atoms although to a lesser extent than in the 1% Cr-substituted alloy.

The compound iron phosphide (Fe_2P) shows interesting magnetic properties. Hexagonal in structure, it is ferromagnetic with a Curie point of 216 K (Wäppling *et al* 1975, Fujii *et al* 1977, Lundgren *et al* 1978) and seems to be quite sensitive regarding the nature of magnetic ordering to metallic substitution of 3d transition-metal elements for iron (see, e.g., Fruchart *et al* 1969, Fujii *et al* 1982, Srivastava *et al* 1987, Dolia *et al* 1988). The substitution of Fe by ferromagnetic metals such as Co and Ni has been reported to stabilize its ferromagnetic behaviour in the sense that the Curie point is raised while the substitution of small amounts of the antiferromagnetic metal Mn lowers the transition point drastically, even changing the ordering to antiferromagnetic. On Cr substitution, we reported in an earlier paper the magnetic behaviour of a series of Cr-substituted compounds $(Fe_{1-x}Cr_x)_2P$ for $x = 0.01, 0.03$ and 0.05 (Dolia *et al* 1988). It was found that even 1% Cr substituted for Fe reduces the magnetic ordering temperature to about 150 K from 216 K in pure Fe_2P. Further substitution of Cr reduces the transition point at a much slower rate. It was also seen that with 1% Cr substitution the system is no longer ferromagnetic. Also such a low level of Cr substitution drastically reduces the hyperfine field at both the metallic sites. In continuation of our earlier work, here we report a study on the compound $(Fe_{0.995}Cr_{0.005})_2P$ in order to examine the influence of a still smaller (namely 0.5%) Cr substitution for Fe on the magnetic behaviour.

The alloy $(Fe_{0.995}Cr_{0.005})_2P$ was prepared following the same procedure as described in our earlier report. The Debye–Scherrer x-ray powder diffraction pattern was recorded using Fe $K\alpha$ radiation. The diffraction pattern confirmed the formation of a single-phase hexagonal alloy. The lattice constants are $a = 5.853$ Å and $c = 3.443$ Å which are in good agreement with the values for pure Fe_2P, namely $a = 5.859$ Å and $c = 3.453$ Å (Wäppling *et al* 1975). Experimental details regarding the bulk magnetization measurements, Mössbauer spectra recording and data analysis have been given previously (Dolia
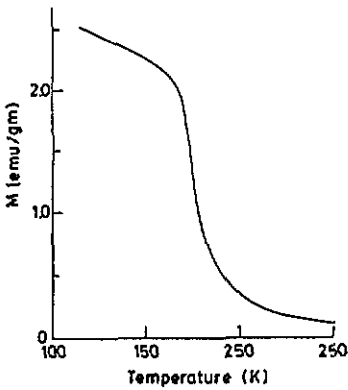
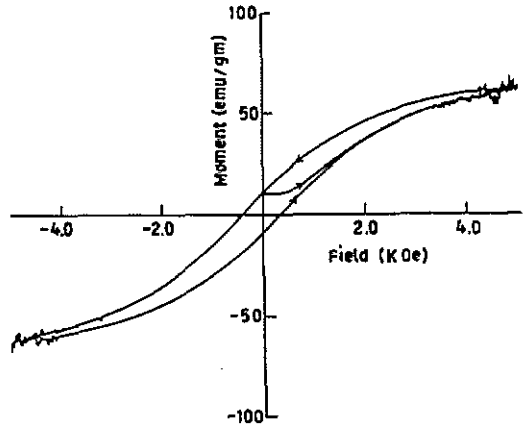**Figure 1.** Magnetization as a function of temperature for $(Fe_{0.995}Cr_{0.005})_2P$ at a field of 100 Oe.

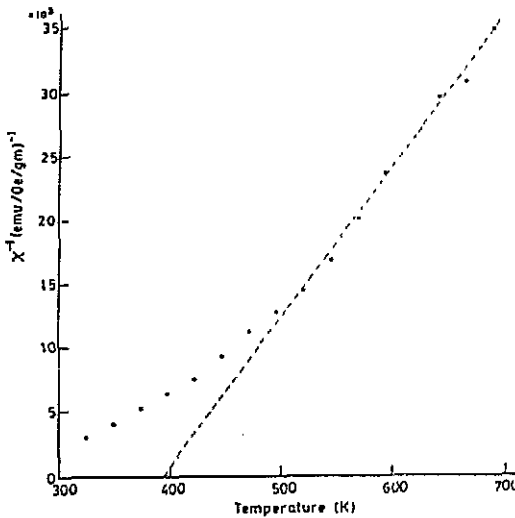**Figure 2.** Magnetization as a function of field for $(Fe_{0.995}Cr_{0.005})_2P$ at 4.2 K.

Figure 3. Inverse susceptibility χ^{-1} as a function of temperature for $(Fe_{0.995}Cr_{0.005})_2P$ in the paramagnetic region at a field of 3 kOe.

et al 1988). In addition, high-temperature magnetization measurements were made using a conventional oven.

Figure 1 shows the magnetization recorded as a function of temperature at a constant field of 100 Oe. The curve clearly shows ferromagnetic behaviour. Unlike the curve for Fe_2P where a sharp transition is observed, in the present case the transition is spread over a wide temperature range. The Curie temperature could be taken as 190 ($\pm$ 10) K which is lower than that of pure Fe_2P (216 K). Further it may be noted that in Ni-substituted Fe_2P alloys as well, which retain ferromagnetic order, the observed magnetic transitions are rather broad and have been classified as a second-order type of transition
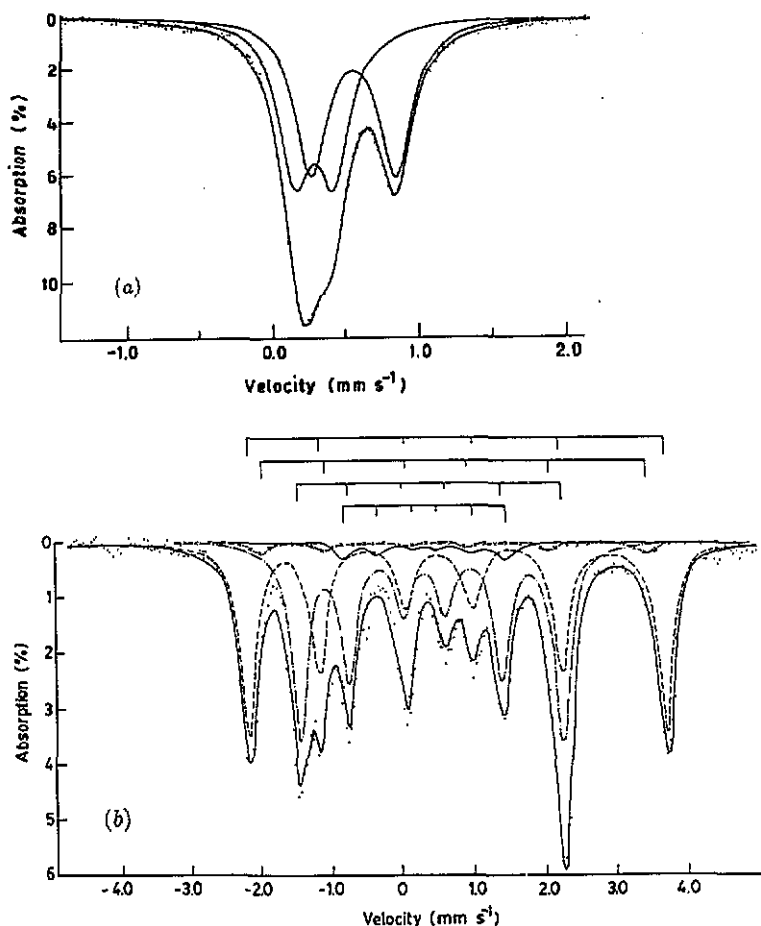
Figure 4. Mössbauer spectra of $(Fe_{0.995}Cr_{0.005})_2P$ at (*a*) 300 K and (*b*) 9 K. The total fitted function and the resolved subspectra are also given.

(Fujii *et al* 1982). However, on the basis of the present measurements alone it is not possible to confirm this for the sample under study.

Figure 2 shows the magnetization recorded at 4.2 K as a function of field up to 5 kOe. A hysteresis loop is observed, further confirming ferromagnetic ordering in this compound. This gives a coercivity of about 0.4 kOe and remanence of 10.4 emu g^{-1}. The sample has a moment of about 60 ($\pm$ 2) emu g^{-1} at 5 kOe which compares well with that for Fe$_2$P (about 45 emu g^{-1}) at the same temperature and field (figure 2 in the paper by Fujii *et al* (1977)). It may be mentioned that Fe$_2$P has a very high uniaxial magnetic anisotropy $K_1 = 2.4 \times 10^7$ erg cm^{-3} (Fujii *et al* 1982). This explains the low value of moment for this compound at 4.2 K and 5 kOe compared with the saturation value of 120 emu g^{-1}. Further, with the substitution of Mn and Ni, K_1 is known to decrease (Fujii *et al* 1982). The fact that the $(Fe_{0.995}Cr_{0.005})_2P$ sample has a higher moment at 5 kOe than Fe$_2$P would suggest that K_1 also decrease on substitution of Cr.

Figure 3 shows a plot of inverse susceptibility χ^{-1} as a function of T for the sample in the range $T > T_C$. A nearly linear variation at higher temperatures shows that the Curie–Weiss law holds for this sample. For T close to T_C, a departure from linearity would arise

Table 1. Mössbauer parameters for $(Fe_{0.995}Cr_{0.005})_2P$: CS, central shift with reference to metallic Fe; DQ, quadrupole splitting, B, Hyperfine field; I, intensity; LW, full width at half-maximum. The accuracies in the parameters CS and LW are within ± 0.01 mm s^{-1}, DQ within ± 0.02 mm s^{-1}, B within ± 0.1 T and I within 2%. The parameters for Fe$_2$P (Wäppling *et al* 1975) are also given for comparison.

x in $(Fe_{1-x}Cr_x)_2P$	T (K)	Fe(1)				Fe(2)				LW (mm s^{-1})
		CS (mm s^{-1})	DQ (mm s^{-1})	B (T)	I (%)	CS (mm s^{-1})	DQ (mm s^{-1})	B (T)	I (%)	
0	300	0.27	0.25	0.0	50	0.54	0.59	0.0	50	0.28
0.005	300	0.30	0.26	0.0	49	0.55	0.56	0.0	51	0.26
0	15	0.41	0.10	11.4	49	0.68	0.19	18.0	51	0.33
0.005	9[a]	0.40	0.08	11.4	47	0.68	0.23	18.1	46	0.28
		0.35	0.00	7.0	04	0.64	0.22	16.7	03	

[a] For both the crystalline sites, the Zeeman patterns with higher B_{hf} and higher intensity would correspond to the SCS of Fe which is comprised of all Fe atoms and the others to the SCS of Fe which consists of all Fe except one Cr. Binomial predictions for the intensities of the two patterns are 47.4% and 2.9% for the Fe(1) site and 46.8% and 2.9% for the Fe(2) site.

because of the existence of short-range order even above T_C. The paramagnetic Curie temperature Θ_p is about 390 (± 10)K; for pure Fe$_2$P it is also reported to be 390 K (Fujii *et al* 1982).

The Mössbauer spectra recorded at 300 and 9 K are shown in figure 4. The spectrum recorded at 300 K does not show Zeeman splitting, in accordance with the fact that the magnetic transition temperature is well below 300 K. As there are two crystallographically non-equivalent metal positions—a tetrahedral site denoted by Fe(1) and a pyramidal site denoted by Fe(2)—the spectrum at 300 K has been analysed into two doublets. The analysed components are also shown in figure 4(*a*). The parameters together with those for Fe$_2$P (Wäppling *et al* 1975) are given in table 1. It is found that the Mössbauer parameters obtained are closely similar to those of pure Fe$_2$P.

Attempts to fit only two six-line patterns to the 9 K spectrum (figure 4(*b*)) did not succeed. The spectrum has been analysed into four six-line patterns on the same lines as discussed in the earlier paper (Dolia *et al* 1988), i.e. two for each of the two crystalline sites. For each site the pattern with the higher internal field (hereafter referred to as B_{hf}) would correspond to a second-coordination sphere (SCS) comprised of all Fe atoms and the other pattern with a smaller B_{hf} would correspond to the SCS consisting of all Fe except one Cr atom. For fitting, the initial guessed parameters for the areas of different patterns were predicted using binomial distributions, keeping in view that Cr preferentially occupies pyramidal (M(2)) site. The final results match these predictions well (cf table 1). The analysed components are shown in figure 4(*b*) together with experimental data. The parameters are given in table 1 together with those for Fe$_2$P at 15 K (Wäppling *et al* 1975). It is seen that at both sites the presence of Cr in SCS of Fe reduces the hyperfine field. A larger reduction for Fe(1) than for Fe(2) correlates with the shorter Fe(1)–M(2) distances (than Fe(2)–M(2)) (Wäppling *et al* 1975). Further, it may be noted that in the 1% Cr-substituted sample the B_{hf}-values (at 80 K) at the Fe(1) site are 9.44 T and 2.23 T, respectively, and at the Fe(2) site they are 15.42 T and 8.61 T, respectively (Dolia *et al* 1988). Thus in the case of 0.5% Cr substitution the magnitude of the reduction in B_{hf} caused by Cr in the SCS is much smaller. Nevertheless, the present

study shows that even 0.5% Cr substituted for Fe has marked influence on the bulk magnetic behaviour (T_C decreasing by about 25 K) and also on the local hyperfine field.

Acknowledgments

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