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Magnetic structure of $(Fe_{0.97}Cr_{0.03})_2P$

SUDHISH KUMAR, S K PARANJPE*, BIPIN K SRIVASTAVA+,
ANJALI KRISHNAMURTHY and V C SAHNI#
Department of Physics, University of Rajasthan, Jaipur 302 004, India
*Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai 400 085, India
#Technical Physics and Prototype Engineering Division, Bhabha Atomic Research Centre, Mumbai 400 085, India
+To whom all correspondence should be addressed

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Abstract. Magnetic behaviour of di-metal iron phosphide with a small substitution of iron by chromium, $(Fe_{0.97}Cr_{0.03})_2P$, has been studied using SQUID magnetometry and powder neutron diffraction. It is paramagnetic at temperatures above ~180 K with persisting short range ferromagnetic (FM) order. At lower temperatures three different regions of magnetic behaviour are identified. FM order evolves in the region 180 K – 120 K but much more slowly and with much less magnetic moments than in Fe_2P. In the region 120 K – 50 K negative exchange interactions gain some importance leading to a loss of FM order. Below 50 K FM interactions again dominate. Pinning centres influence the behaviour at low temperature up to ~100 K.

Keywords. Magnetic structure; neutron diffraction; alloys.

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1. Introduction

The di-metal iron phosphide Fe_2P, crystallizing in a hexagonal C22 structure with $P\bar{6}2m$ (D^3_{3h}) space group, is a ferromagnet with a sharp transition to paramagnetic state at ~ 210 K [1]. It has a high uniaxial magnetic anisotropy with the magnetic moments aligned along [001] and exhibits a metal like electrical conductivity (resistivity $\sim 10^{-4}$ ohm cm [2]). The magnetic behaviour of the material has been extensively studied for the effect of pressure and metallic substitutions as well as vacancy substitutions [1–7 and references therein]. All these are known to exhibit strong influences. Thus, application of hydrostatic pressure reduces Curie temperature with pronounced anisotropy and above 5 kbar double metamagnetic transitions occur – first from ferromagnetic (FM) to metamagnetic and then to antiferromagnetic state in the sequence of decreasing temperature [e.g., 1 and references therein].

Metallic substitutions, the subject of the present paper, also lead to interesting changes. Small substitutions of Fe by Co, as also by Ni, strengthen the FM structure as revealed in the elevation of Curie temperature, e.g., from ~210 K in Fe_2P to ~295 K in 5% Ni substituted alloy [8]. On the other hand substitutions by Cr and Mn, tend to destroy the FM order; at as low a level of substitution as 3% of Mn, and also of Cr, the bulk magnetization is considerably reduced [9,10], as compared to that in Fe_2P.

In an earlier study on the title alloy, our group [10] reported magnetization measurements as a function of magnetic field (in fields > 500 Oe) and temperature. However, due to the use of liquid nitrogen, the low temperature range was limited to 80 K. Only one peak was seen in magnetization-temperature curve. It was surmised that ferromagnetic order does not exist but no further inference could be made about the magnetic behaviour. More recent studies by Srivastava *et al* [6] on an alloy formed of simultaneous substitutions by Cr and Ni in small proportions have shown the existence of re-entrant spin glass phase. This has lead to a greater interest in examining the magnetic behaviour of the Cr substituted alloy and this paper is an effort in that direction. Magnetization and neutron diffraction measurements have been performed on poly-crystalline sample of $(Fe_{0.97}Cr_{0.03})_2P$ in the temperature range 5 K–300 K. It is found that as the temperature is lowered from 300 K, it exhibits three different kinds of magnetic behaviour in three temperature ranges. The plan of the paper is as follows. The experimental details are given in the next section. Results and discussions are presented in the subsequent sections.

2. Experimental details

The alloy has been prepared by the method of solid state diffusion at ~1000°C. The details of preparation are described elsewhere [10]. Phase identification was done with the help of X-ray diffraction patterns recorded on a Philips powder diffractometer (model PW 1840) using FeK_α radiation. All the observed reflections could be indexed using Fe_2P like hexagonal cell.

Magnetization measurements have been made using a SQUID magnetometer (quantum design model MPMS) for both zero field cooled (ZFC) as well as field cooled (FC) conditions covering a temperature range of 5 K to 300 K. In ZFC mode the sample was cooled under zero field from 300 K to 5 K, then a magnetic field was applied and magnetic moment of the sample was measured as a function of temperature (T) in the warming cycle. In FC mode the sample was cooled from 300 K to 5 K in the presence of field and M vs T was recorded during cooling cycle.

Magnetization has also been measured as a function of the external magnetic field at different sample temperatures. These measurements were made as follows. The sample was first cooled from 300 K (paramagnetic state) to 10 K under zero field. Then successively increasing fields were applied and magnetization was recorded at each field value. After thus completing the measurements at one temperature (10 K) the field was switched off and sample was warmed to 300 K. It was kept at 300 K for about half an hour and then cooled to the next temperature 30 K. The magnetization measurements were once again made under successively increasing fields. After the measurement the field was again switched off and the sample was warmed up to 300 K. This process was continued in the above manner going over different temperatures.

Neutron diffraction measurements have been made at the 100 MW 'Dhruva' reactor, Bhabha Atomic Research Centre, Mumbai, using profile analysis powder diffractometer with a position sensitive detector. A beam of $\lambda = 1.09$ Å was used. For low temperature measurements, from 300 K down to 10 K, a closed cycle refrigerator cryostat (Air Products make) was used. The data was recorded with 10 gm of powdered sample placed in cylindrical vanadium or aluminium can. Patterns have been recorded in 2θ range of 10° to 40° at seven different temperatures of 10 K, 45 K, 75 K, 100 K, 120 K, 150 K and 300 K.

3. Results

Figures 1(a) and 1(b) show magnetization measurements in the presence of external fields of 20 Oe and 200 Oe respectively. Results are shown for both ZFC as well as FC modes. Two maxima appear, one at ~50 K and another one at ~120 K. Two points are worth noting. The ZFC and FC curves depart from each other over the entire temperature range. As the field is increased, the FC curve flattens out at lower temperatures.

Figures 2(a) and 2(b) depict the variation of magnetization (M) as a function of external magnetic field (H) at different temperatures. Some notable features of figure 2 can be easily identified. (a) The M–H curve at 10 K lies the lowest. (b) The M–H curve at 30 K is substantially higher than the 10 K curve. (c) If we examine the M–H curve at 30 K, we find that it begins to increase somewhat rapidly above about 3 kOe. Similar field values for 43 K, 57 K and 72 K data can be identified as 4 kOe, 5 kOe and 5 kOe respectively. This feature is not observed for temperatures 100 K and above.

Figure 3 shows the neutron diffraction pattern at 300 K. The pattern analysed using Rietveld profile refinement technique [11] further confirms the single phase nature and also the stoichiometry of the sample. Table 1 gives the refined parameters obtained from the Rietveld analysis. One result of significance is that out of the two metallic sites – tetrahedral M1 (surrounded by 4 P atoms) and pyramidal $M2$ (surrounded by 5 P atoms)

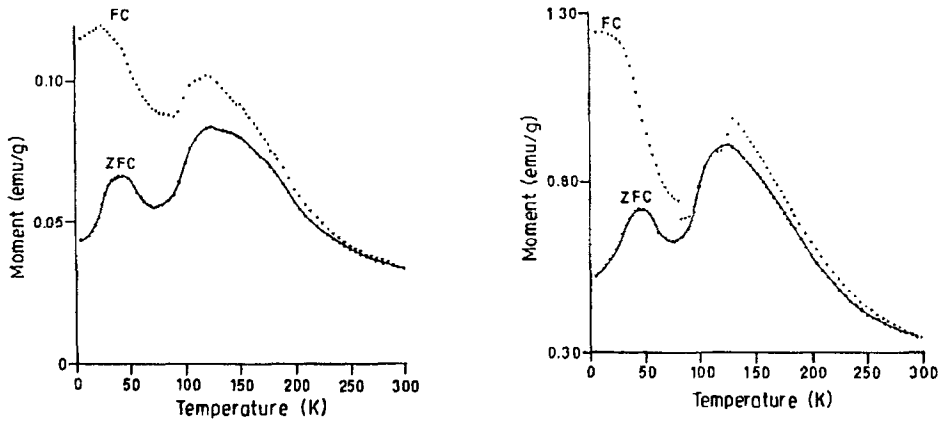
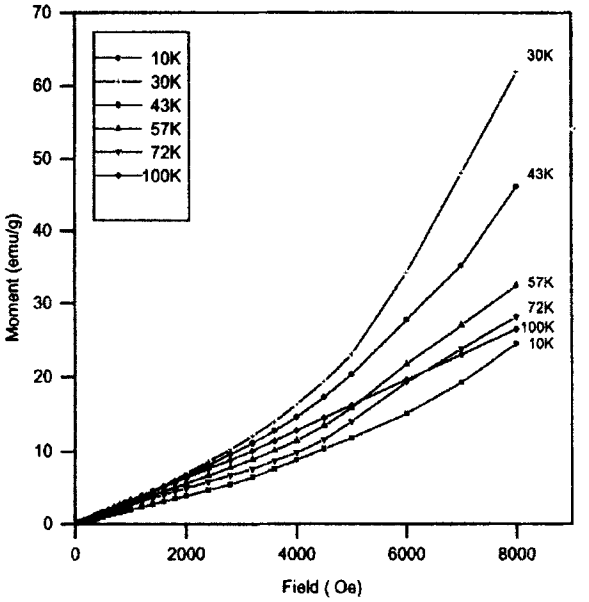
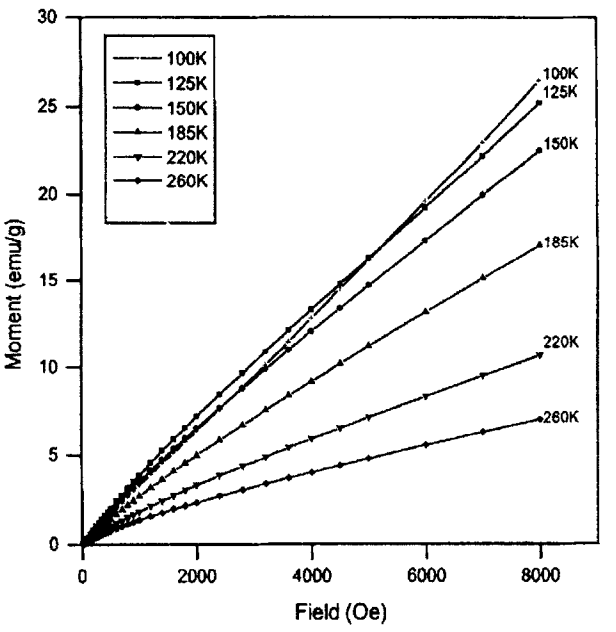


Figure 1. Magnetic moment, recorded in zero field cooled (ZFC) and field cooled (FC) modes as function of temperature under external magnetic field of (**a**) 20 Oe and (**b**) 200 Oe.



(a)



(b)

Figure 2. Magnetic moment as function of external magnetic field at different temperatures in the range (**a**) 10 K–100 K and (**b**) 100 K–260 K.

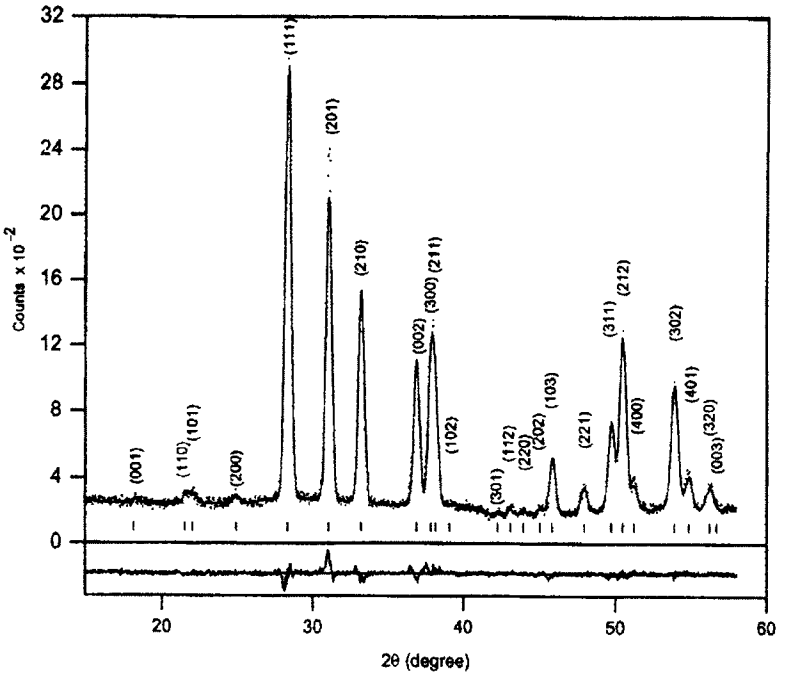


Figure 3. Neutron diffraction pattern at 300 K. Observed (calculated) profiles are given by the dotted (solid) curves. The short vertical marks represent the Bragg reflections. The lower curve is the difference plot.

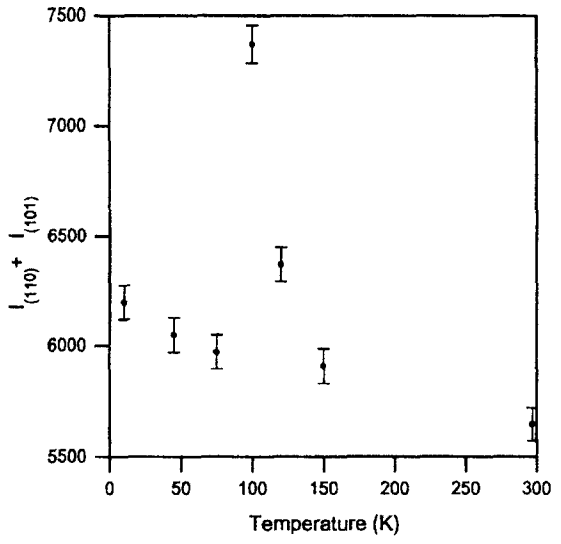
Table 1. Results of the profile refinement of the neutron diffraction data on $(Fe_{0.97}Cr_{0.03})_2P$ at 300 K

Space group = $P\bar{6}2m$;	$a = 5.836(2)$Å,	$c = 3.453(1)$Å
Site	x	Occupation
$3f$ (x 0 0)	0.2602(4)	Fe
$3g$ (x 0 1/2)	0.5937(4)	0.94 Fe + 0.06Cr
$2c$ (1/3 2/3 0)	–	0.6667P
$1b$ (0 0 1/2)	–	0.3333P

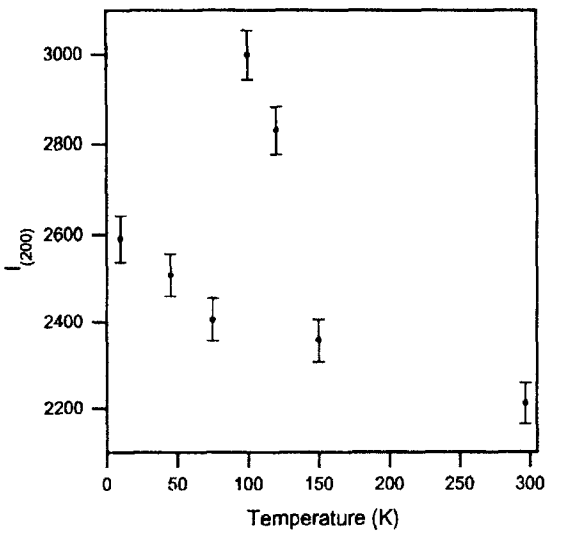
R- factors: $R_p = 5.84$, $R_{wp} = 7.45$ and $R_{\text{expected}} = 5.14$

– Cr occupies the $M2$ site with a total preference. This is in conformity with the reported Mössbauer result at higher Cr substitutions [12].

Patterns recorded at lower temperatures down to 10 K do not give signature of any additional reflection but relative changes occur in intensities of some of the reflections at different temperatures. The magnetic contribution is large for the reflections (110), (101) and (200). Figure 4(a) plots sum of the integrated intensities [13] of (110) and (101) as a function of temperature and figure 4(b) plots the variation for the reflection (200). It is noticed that coming from the high temperature side the magnetic scattering first increases peaking at ~100 K, then drops quite much and again starts increasing at ~75 K downwards.



(a)



(b)

Figure 4. Integrated intensity as function of temperature for reflections (a) (110) + (101) and (b) (200).

4. Discussion

Starting at 300 K the alloy must definitely be in the paramagnetic state. However, the observed difference between FC curve and the ZFC one right up to 300 K (figure 1) is suggestive of the fact that short range order persists well above the transition temperature. Certainly in Fe_2P, short range order is known to persist as high temperatures as $\sim 3T_c$ [14,15].

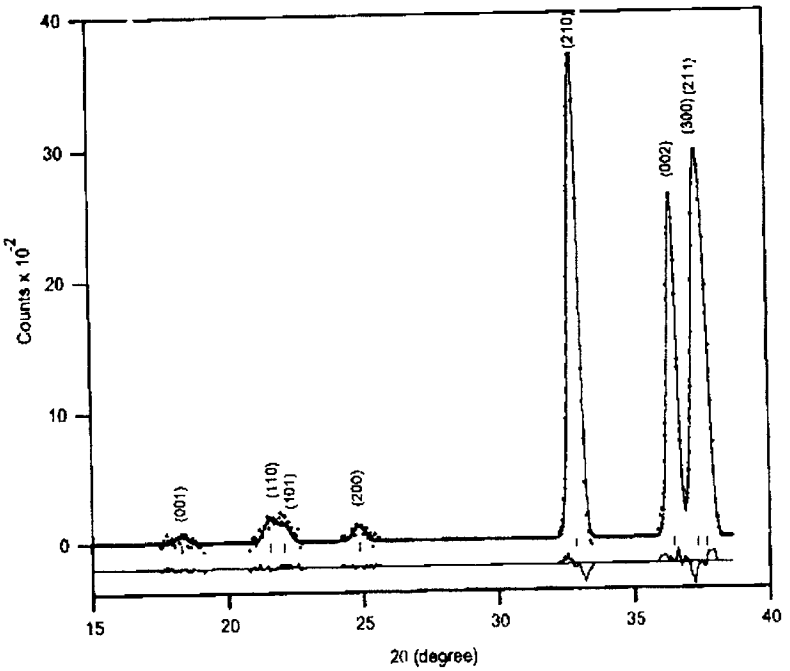


Figure 5. Neutron diffraction pattern at 100 K (the peaks corresponding to (111) and (201) reflections have been excluded as contributions from Al sample holder overlap in this region). Observed (calculated) profiles are given by the dotted (solid) curves. The short vertical marks represent the Bragg reflections. The lower curve is the difference plot.

Regarding the situation at lower temperatures, as discussed in the following, as the material is cooled it exhibits three different kinds of magnetic behaviour. One point that is quite clear is that the material does not show antiferromagnetic order at any temperature. This is borne out of the fact that in the neutron diffraction patterns no additional reflection shows up at any temperature (below 300 K) down to 10 K. As the sample is cooled, a magnetic order does evolve and we identify the onset of first transition with a temperature (T_c) ~180 K around which a change of slope is seen in the ZFC $M-T$ curve in lower field (cf. figure 1(a)). In the region 180 K > T > 120 K an enhancement occurs in magnetization as well as in magnetic scattering suggestive of increasing ferromagnetic order. It is to be noted, however, that magnetization under an external magnetic field of 8 kOe is much less in the present case as compared to that for Fe_2P [9]. For obtaining the moments for the tetrahedral Fe_1 and the pyramidal Fe_2 sites, the diffraction pattern at 100 K (the temperature at which the magnetic contribution to Bragg peaks is maximum) was refined (using Hewat profile refinement program [16]). (The moments were assumed to be aligned along c-axis as in Fe_2P and form factors used were those for Fe^0 and Fe^{+4} for Fe_1 and Fe_2 sites respectively [17]). The observed and fitted profiles are shown in figure 5. The refinement gives Fe_1 and Fe_2 moments as 0.21(3) μ_B and 0.51(27) μ_B respectively. These values of the moments are much less than those in Fe_2P. The large error levels in the obtained values, particularly for the site Fe_2, may suggest that the assumption of the moments pointing

along c-axis does not entirely hold.

On further lowering of temperature the M versus T curves (figure 1) give evidence of two more transitions – one at ~120 K and the other at ~50 K. Neutron diffraction (ND) also confirms the occurrence of these transitions (figure 4). However, due to small number of points in figure 4 particularly around the transition at higher temperature the uncertainty in this transition temperature is larger in ND measurement and is seen at somewhat lower temperature of ~100 K. An observation worth noting is that while at the first of these two transitions the magnetic scattering drops considerably, below the second one it keeps increasing with lowering of temperature. These features are in contrast to those seen in Fe_2P. At the first transition this is indicative of some loss of ferromagnetic order and therefore of negative exchange gaining some importance, but at the same time, not so dominating as to give rise to an antiferromagnetic order. The fact of both the magnetization and the magnetic scattering enhancing below ~70 K, i.e., around the second transition, is suggestive of again a pre-dominance of the positive exchange in this temperature region. We assign the second transition at ~50 K to this feature. The other important observations concerning the temperature region below ~70 K are: (i) magnetization in the FC mode, even in a low field of 20 Oe, shows large increase (over ZFC mode) and in a field of 200 Oe the peak at ~50 K flattens out when M is recorded in the FC mode, (ii) (intensity of) neutron magnetic scattering, recorded in zero field, continuously increases with decreasing temperature and does not show any peak and at the same time even at 10 K it is lower than at ~100 K and (iii) slopes of the M–H curves at various temperatures show an increase at different fields. These observations together are suggestive of a feature that at lower temperatures the domain walls are somewhat pinned resulting in a shorter range of FM order and they become unpinned as the temperature is raised and also as, at a given temperature, the external magnetic field is increased. The fact that the last of the three observations noted here continues right up to ~100 K, suggests that the domain walls continue to remain pinned till ~100 K.

To summarize, we infer that indeed substitution of just 3 atomic % of Fe by Cr in Fe_2P considerably weakens the ferromagnetic order and gives rise to a complicated magnetic behaviour. Four different regions of magnetic behaviour have been identified. (i) Above ~180 K the state is a paramagnetic one with persisting short range order. (ii) In the region 180 K $> T >$ 120 K, ferromagnetism begins to evolve but much more slowly than as reported in Fe_2P and with much smaller moments at the two sites. (iii) In the region 120 K $> T >$ 50 K, negative exchange interactions become important (but not enough as to give rise to anti-ferromagnetic order). (iv) Finally, below 50 K ferromagnetism is again predominant but with domain walls being pinned. (The observation concerning the pinning of domain walls continues till ~100 K.)

Now, as described in §1, the magnetic behaviour of Fe_2P has been reported to be quite sensitive to external pressure, stoichiometry as well as to substitutions. Calculations on electronic structure show that Fermi energy lies nearly on a peak of the density of state curve which results in this sensitive nature [18]. Another explanation forwarded is in terms of the strength of exchange interaction for different metal-metal bonds in Fe_2P. In this material, for the tetrahedrally ($M1$) and pyramidally ($M2$) coordinated atoms, there are in all four different metal-metal distances and it has been suggested/inferred that $M1$–$M1$ (2.60 Å) has a strong −ve exchange, $M1$–$M2$ (2.63 Å and 2.71 Å) have strong +ve exchange and $M2$–$M2$ (3.08 Å) has a weak −ve exchange [2,3]. A tentative explanation for the observed behaviour in the 3% Cr substituted alloy can be envisaged in terms

of this description invoking the relative strengths of exchange interactions. Introduction of Cr, which goes to pyramidal $M2$ site and which is bigger in size than Fe, should result, for $M1$–$M2$ and $M2$–$M2$ bonds, in reduction of the ratio R/r of inter-metallic separation R to sum r of the metallic radii. This leads to an overall weakening of the FM behaviour. Results on the present alloy then suggest that in this less strongly (than stoichiometric Fe_2P) FM system, lowering of temperature plays a crucial role. At ~120 K the (one corresponding to) 2.63 Å bond, which is quite close in length to the (strongly −ve exchange) 2.60 Å bond, also attains a −ve (or a much weakened +ve) exchange becoming more so at lower temperatures. At the same time results also suggest that successive lowering of T, the reduction in R/r for the other +ve exchange $M1$–$M2$ bond (of length 2.71 Å) makes it more and more +ve. And at ~70 K, the balance of these opposing trends is such that the system again begins to show an increased FM nature (as compared to the region of 120 K–70 K).

Finally, however, since the neutron magnetic scattering in this material is quite weak – the intensity at the peak point (of ~100 K) itself being rather small – it is not possible on the basis of the present results to have a deeper understanding of the magnetic structure and more work would be needed for further unravelling of the structure.

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References

[1] O Beckman and L Lundgren, in *Handbook of magnetic materials*, edited by K H J Buschow (Amsterdam, Elsevier, 1991) Vol. 6
[2] H Fujiwara, H Kadomatsu, K Tohma, H Fujii and T Okamoto, *J. Magn. Magn. Mater.* **21**, 262 (1982)
[3] H Fujii, T Hokabe, H Fujiwara and T Okamoto, *J. Phys. Soc. Jpn.* **44**, 96 (1978)
[4] V Ghose, N Sivayogan, A Krishnamurthy, B K Srivastava and S N Dolia, *J. Appl. Phys.* **73**, 5701 (1993)
[5] S I Khartsev, L I Medvedeva and E A Zavadskii, *J. Magn. Magn. Mater.* **111**, 189 (1992)
[6] B K Srivastava, A Krishnamurthy, V Ghose, J Mattsson and P Nordblad, *J. Magn. Magn. Mater.* **132**, 124 (1994)
[7] E A Zavadskii, L I Medvedeva and A E Filippov, *J. Magn. Magn. Mater.* **43**, 53 (1984)
[8] S N Dolia, A Krishnamurthy, V Ghose and B K Srivastava, *J. Phys.: Condens. Matter* **5**, 451 (1993)
[9] H Fujii, T Hokabe, K Eguchi, H Fujiwara and T Okamoto, *J. Phys. Soc. Jpn.* **51**, 414 (1982)
[10] S N Dolia, A Krishnamurthy and B K Srivastava, *J. Phys.* **C21**, 6005 (1988)
[11] H M Rietveld, *J. Appl. Cryst.* **2**, 65 (1969)
[12] R Fruchart, A Roger and J P Senateur, *J. Appl. Phys.* **40**, 1250 (1969)
[13] For obtaining the intensities, Gaussian functions were fitted to the profiles of the different reflections. The intensities have been normalized as per that of the reflection (210) as this reflection is mainly nuclear (the magnetic contribution to its intensity is negligible (< 2%))
[14] S Komura, K Tajima, H Fujii, Y Ishikawa and T Okamoto, *J. Magn. Magn. Mater.* **15-18**, 351 (1980)
[15] C Wilkinson, R Wappling and K R A Ziebeck, *J. Magn. Magn. Mater.* **78**, 269 (1989)

[16] A W Hewat, *Harwell Report* **74**, H 62 S (1974)

[17] H Fujii, S Komura, T Takeda, T Okamoto, Y Ito and J Akimitsu, *J. Phys. Soc. Jpn.* **46**, 1616 (1979)

[18] O Eriksson, J Sjoström, B Johansson, L Häggström and H L Skriver, *J. Magn. Magn. Mater.* **74**, 347 (1988)