

Crystal structure and magnetic properties of some MM'X pnictides investigated by neutron diffraction and magnetisation measurements

A. Koumina^{1,3}, M. Bacmann², D. Fruchart², M. Mesnaoui³, P. Wolfers²

¹Laboratoire de Physique, Ecole Normale Supérieure, BP 2400, Marrakech, Morocco.

²Laboratoire de Cristallographie, CNRS, BP 166 - 38042 Grenoble Cedex 09, France.

³Laboratoire de Chimie du Solide Minéral, Faculté des Sciences-Semlalia, BP 2390, Marrakech, Morocco.

In order to analyse the magnetic structure and to point out potential relationships between the structural parameters and magnetic behaviour, *in situ* powder diffraction experiments were investigated for three specific compounds and systems MM'X. The study was carried out also by using magnetisation measurements. These investigations are supported by electronic structural calculations analyses carried out in parallel to this work.

I. Introduction

The transition metal ternary pnictides MM'X (M, M' = 3d transition elements and X = As, P) exhibit a large variety of magnetic properties. They crystallize in three different types of structure: Fe₂P (hexagonal, $P\bar{6}2m$), Fe₂As (tetragonal, $P4/nmm$), Co₂P (orthorhombic, $Pnma$). All these structures contain two atoms polyhedra, which form the coordination of metal atoms in tetrahedra (t) and square-pyramidal (p) sites [1]. Recently, a new promising material was discovered [2], namely the transition-metal system MnFe(As_(1-x)P_x), which exhibits a giant magnetocaloric effect (MCE) just above the room temperature at the composition $x=0.45$. This observation is of significant technological relevance since it identifies these compounds as potential candidates for magnetorefrigerant application. Nowadays, there is much interest in magnetic refrigeration, as it offers the prospect of an energy efficient and environment friendly alternative for the traditional vapour-cycle refrigeration technique. The development of magnetic cooling near room temperature requires basic research into the exploration and characterisation of new magnetic refrigerants, as well as into the design of new magnetic-refrigeration devices. The previous studies on the structural and magnetic properties of phosphides MM'P [3], arsenides MM'As and arsenio-phosphides MM'(P_{1-x}As_x) [4-7] showed that the ferromagnetism of intermetallic compounds MM'X is stabilized for an average electronic configuration close to that of Fe₂P.

In this work, three isostructural hexagonal compounds, isoelectronics of Fe₂P, i.e. MnFeAs,

CrNiAs..., were selected in relation to their marked magneto-elastic properties and are considered according to the most interesting correlations between structural and magnetic properties.

The studies were mainly carried out using neutron diffraction and magnetisation measurements. The *ab initio* electronic structure calculations were carried out by the Korringa-Kohn-Rostocker (KKR) method [8,9] using low-temperature experimental values of the lattice parameters and atomic coordinates deduced from the neutron refinements.

II. EXPERIMENTAL METHOD

Magnetic measurements on powder samples were performed using a magnetometer in "Laboratoire des Champs Magnétiques Intenses - Max Planck Institute (CNRS, Grenoble, France)", with magnetic field of 0.1 and 10 T, in the temperature ranging from 5 to 300 K. The neutron diffraction experiments on the polycrystalline samples were carried out on the D1B diffractometer installed at the High Flux Reactor ($\lambda = 2.526 \text{ \AA}$) in the Laue Langevin Institute (ILL, Grenoble, France) at $5 \text{ K} < T < 250 \text{ K}$. The crystal and magnetic structures were refined with the MXD program [10]. A Gaussian peak shape function was used to fit the intensities of the peaks using the ABF fit program [11].

III. RESULTS AND DISCUSSION

III.1. Fe₂P: Crystal structure of Fe₂P compound was refined from the neutron diffraction data (Fig. 1). It has a hexagonal structure, with space group

$P\bar{6}2m$. Iron atoms occupy two crystallographically inequivalent sites: pyramidal (3g) and tetrahedral (3f). The refined structure parameters (Table 1) were in good agreement with those obtained by X-rays on single crystal [12]. Magnetic studies of Fe_2P have been performed by many investigators [12-15], but there are considerable disagreements in the magnetic properties. These discrepancies lead us to carry out a detailed study of magnetic properties of this compound. At 6 K, the measured atomic moments of tetrahedral Fe(3f) and pyramidal Fe(3g) sites are respectively $0.59(2) \mu_B$ and $2.22(1) \mu_B$, resulting in a net moment of $2.82(3) \mu_B$. From this refinement, the resulting ferromagnetic moment is in good agreement with the magnetisation measurement ($H=150$ kOe, $T = 4$ K) giving a value of approximately

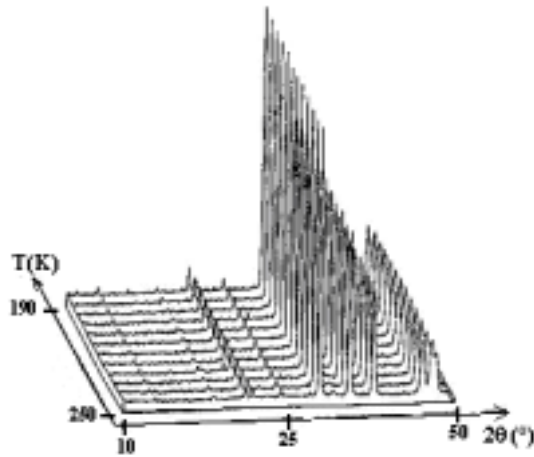


FIG. 1: 3-D plot of the neutron diffraction patterns of Fe_2P compound (190-250 K).

Atom	x	y	z	a(Å)	c(Å)
Fe(3g)	0.595 ₃	0	1/2	5.872 ₁	3.460 ₁
Fe(3f)	0.258 ₀	0	0		
P(2c)	1/3	2/3	0		
P(1b)	0	0	1/2		

Table 1. Refined lattice parameters and atomic positions from neutron powder diffraction data at 295 K.

$2.87(3) \mu_B$ and with our KKR calculations ($0.80 \mu_B$ for Fe(3f) and $2.33 \mu_B$ for Fe(3g)) [16].

In our previous paper [16,17], The magnetisation measurements and the thermal evolution of the magnetic moments of the diffraction patterns of both sites of iron presents a brutal fall in the vicinity of T_c . This abrupt decrease and the discontinuity of the cell parameters at T_c is a strong indicating that the ferro-paramagnetic transition is of the first order in this compound.

It can be concluded that the disagreements in the magnetic properties are due mainly to the fact that Fe_2P compound can present variations of stoichiometry formula ($Fe_{2-\epsilon}P$).

III.2. CrNiAs : The crystal structure parameters of CrNiAs refined from the neutron diffraction (Fig. 3) are reported in Table 2. The refinements revealed that the crystallographic ordering of Cr and Ni atoms is complete in CrNiAs compound; Cr and Ni are located in pyramidal and tetrahedral sites, respectively.

Atom	X	y	z	a(Å)	c(Å)
Cr(3g)	0.572 ₉	0	1/2	6.108 ₁	3.656 ₁
Ni(3f)	0.251 ₅	0	0		
As(2c)	1/3	2/3	0		
As(1b)	0	0	1/2		

Table 2. Refined lattice parameters and atomic positions from neutron powder diffraction data.

The temperature dependence of the cell parameters analyzed by powder neutron diffraction from 250 to 1.5 K, reveal two transition temperatures.

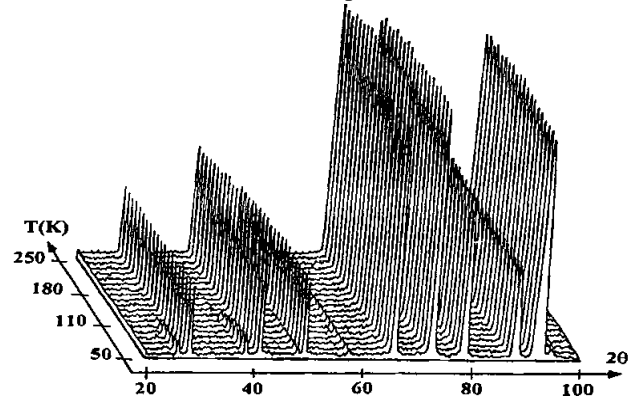


FIG. 2: 3-D plot of the neutron diffraction patterns of CrNiAs compound (50 - 250 K).

The first one, at the Curie temperature $T_c = 182$ K, is not accompanied by structural modification while at the second transition at 110 K, the cell parameters present a strong change of slope. The anomalies of the temperature dependence of the lattice parameters near the transitions are caused by a magnetoelastic effect.

Our preliminary study of magnetic properties of this compound has permitted to point the existence of three magnetic domains. For $T > 182$ K, CrNiAs is paramagnetic, in the range $110 \text{ K} < T < 182 \text{ K}$ it behaves ferromagnetically ordered and below 110 K the magnetic behaviour appears more complicated than that of a simple ferromagnet. Earlier, the magnetic structure of CrNiAs was analyzed with a ferrimagnetic arrangement collinear to the c-axis with $0.55 \mu_B$ on Cr and -0.65

μ_B at 110 K, in agreement with the experimental saturation magnetisation of $1.3 \mu_B/\text{f.u.}$ [18]. More recently precise neutron diffraction experiments lead to a ferromagnetic arrangement collinear to the c-axis with the respective values of $1.25(5) \mu_B$ for Cr and $0.15(5) \mu_B$ for Ni [19]. This simple arrangement is stabilized for temperature ranging from 182 to 110 K. The ferromagnetic behaviour of CrNiAs is mainly due to Cr atoms, the Ni atoms exhibiting a negligible magnetic moment ($< 0.2 \mu_B$). Both the saturation magnetisation measurements and the KKR band calculations were found in close agreement with the second type of ferromagnetic configuration.

At lower temperatures ($T < 110$ K), additional and sine in-plane components have been refined [20]. Such a more complicated oscillating magnetic structure can be described on the basis of an ortho-hexagonal cell ($a_H\sqrt{3}$, a_H , c_H) and an incommensurate magnetic propagation vector $\vec{q} = (0, 0, q_z)$, with $q_z = 0.228$. More complicated combinations can be proposed and several models were tested. Analysis of the intensity of the magnetic reflexions for the incommensurate structure indicates that a slightly better value of the reliability factor ($R = 3.4\%$) is obtained for a sine-modulated magnetic structure. A similar type of magnetic structure is observed in the isostructural MnRhAs compound [21].

III.3. MnFeAs: The MnFeAs compound which is stable in tetragonal form (F_2As type, $P4/nmm$) has been stabilized under high pressure and high temperature (3.5 GPa, 800 °C) in the hexagonal phase (Fe_2P type, $P\bar{6}2m$).

The structural parameters refined from neutron diffraction patterns are reported in Tables 3 and 4. The refinements revealed that the crystallographic ordering is complete in the both phases of MnFeAs, i.e., iron and manganese are located on tetrahedral and pyramidal sites, respectively [22]. This is in agreement with previous Mössbauer spectroscopy investigations [23].

Atom	x	y	Z	a(Å)	c(Å)
Mn(2c)	0	1/2	0.332 ₁	3.7425 ₃	6.0292 ₃
Fe(2a)	0	0	0		
As(2c)	0	1/2	0.744 ₁		

Table 3. Refined lattice parameters and atomic positions from neutron powder diffraction data of MnFeAs tetragonal type at 250 K.

The tetragonal phase is antiferromagnetic ($T_N = 470$ K) with the magnetic cell doubled along c-axis, with respect to the chemical one.

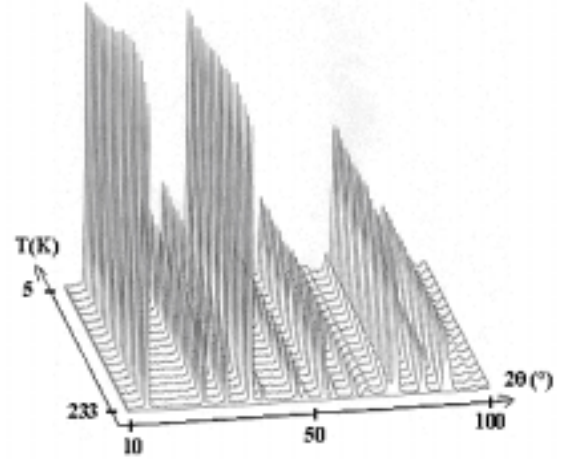


FIG. 3: 3-D plot of the neutron diffraction patterns of MnFeAs tetragonal type (5 - 233 K).

Atom	x	Y	z	a(Å)	c(Å)
Mn(3g)	0.593 ₂	0	1/2	6.24907 ₅	3.60497 ₆
Fe(3f)	0.2530 ₉	0	0		
As(2c)	1/3	2/3	0		
As(1b)	0	0	1/2		

Table 4. Refined lattice parameters and atomic positions from neutron powder diffraction data of MnFeAs hexagonal type at 250 K.

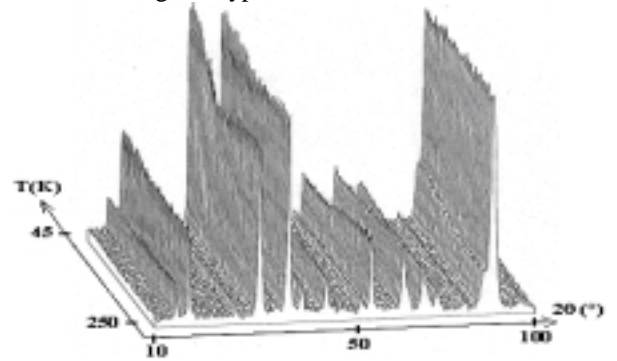


FIG. 4: 3-D plot of the neutron diffraction patterns of MnFeAs hexagonal type (45 – 250 K).

The local magnetic moment on Mn(2c) refined at 5 K from the neutron study is $3.36(2) \mu_B$, while no magnetic significant magnetic moment is observed on the Fe(2a) site. Figure 4 shows the thermal evolution of the magnetic moment of the diffraction patterns on Mn(2c) site.

The hexagonal phase is ferromagnetic with Curie temperature T_c near 190 K. The magnetic moments

determined by neutron diffraction are $3.14(2) \mu_B$ and $1.54(3) \mu_B$ on Mn(3g) and Fe(3f), respectively.

The resulting moment is $4.6 \mu_B$. This result is in good agreement with the saturation magnetisation of $4.5 \mu_B/\text{f.u.}$ measured at 5 K applying a magnetic field as large as 10 T.

The band structure study of the tetragonal MnFeAs shows DOS splitting exclusively on the Mn(2c) sites, resulting in the local magnetic moment of $3.42 \mu_B$, unlike the hexagonal type where the magnetic moments of $3.13 \mu_B$ and $1.10 \mu_B$ are found on Mn(3g) and Fe(3f), respectively. These values show a fair agreement between the magnetic measurements and KKR calculations.

Two remarks can be made concerning possible correlations between the structure transformation and the magnetic characteristics.

Firstly in the tetragonal compound where manganese is coordinated by a consequent number of manganese atoms (50% Mn, 50% Fe), dominant Mn-Mn antiferromagnetic couplings can result from this coordination as in most part of the manganese rich intermetallics. It is different after the compound is transformed to the hexagonal MnFeAs: the Mn metal coordination is dominantly of iron type. If the conditions of stabilisation of a ferromagnetic moment on the iron (tetrahedral) site exists, the long range magnetic ordering should be of ferromagnetic type through both (tetrahedral)-(tetrahedral), (tetrahedral)-(pyramidal) couplings namely.

Secondly, if one considers that the local magnetic moment may depend for a part from the mean distance between the central atom and the shell of the next neighbour metal atoms (atomic volume dependence), typical variations could result from the increase and decrease respectively of the $\langle \text{Fe-M} \rangle$ and $\langle \text{Mn-M} \rangle$ distance with the high pressure transformation. Figure 5 shows that the correlations between the mean-metal distances and the local moments are fairly good.

IV. CONCLUSION

Our analysis by neutron diffraction of Fe_2P compound regarding the dilatometric study and the determination of the magnetic moments evolution with temperature showed that the first order ferro-paramagnetic phase transition is associated with the discontinuous change in the parameters of the hexagonal unit cell. At this transition ($T_C = 217 \pm 2 \text{ K}$), this analysis showed that with a strong magnetoelastic transition around T_C , could correlate the effect of important discontinuities of the cell parameters with the reduction of magnetism on the two iron sites. The transition of ferro to paramagnetism occurs with a spontaneous and marked reduction moment of mainly iron in pyramidal site. The whole study deferred in this work confirms the existence of a narrow correlation between structural, magnetic and electronic properties.

The isoelectronic CrNiAs arsenide, isostructural of Fe_2P , whose behavior at low temperature reveal the relative instability of ferromagnetic arrangement, phenomenon

raised in addition with Fe_2P during weak substitution carrying on iron, or by application of an external pressure.

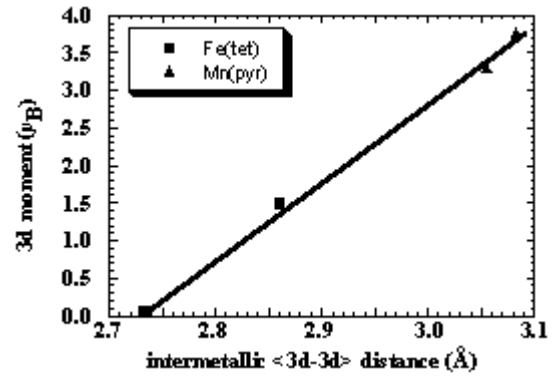


FIG. 5: Magnetic moments in the tetragonal and hexagonal MnFeAs versus mean $\langle \text{M-M} \rangle$ distance.

Such instability was also recorded previously with another isoelectronic compound like MnRhAs.

The criteria of order (steric and electronegativity) were initially checked in experiments: they are applied here with a perfectly established chemical order. A second contribution to the study of CrNiAs was to measure accurately the evolution of the cell parameters and volume with temperature, to determine the magnetic structure of made up on both sides of an abrupt magnetoelastic transition at 110 K, and finally to connect these characteristics to measurements of magnetization carried out in parallel.

In the light of the electronic structural analyses, it is clear that stability (or instability) of the total ferromagnetism of the compound depends on the polarization of the local moments with a change measured about $0.8 \mu_B$ of the moment measured on chromium at the time of the magnetoelastic transition. At low temperature, magnetic arrangement is of type modulated at incommensurable intervals, according to the c-axis.

The $\text{MnFe}(\text{P}_{1-x}\text{As}_x)$ system was studied at the same time for the intermediate compositions (hexagonal, $\text{P}\bar{6}2\text{m}$) and for compositions rich in arsenic (tetragonal, P4/nmm). Here still and for all the compositions, the chemical order was checked and obeys perfectly of the two criteria of selectivity of pyramidal and tetrahedral sites.

For the second series of studied compositions, the tetragonal compound can be stabilized in the hexagonal form after application of a pressure of 3.5-4 GPa at high temperature. MnFeAs in tetragonal form is antiferromagnetic. It is transformed under pressure into the denser hexagonal form, which appears ferromagnetic. This analysis which is carried out on the experimental level reveals that magnetic moments of manganese and iron (determined by neutrons and measurements of magnetisation) vary linearly with

the evolution of the average intermetallic distances calculated on the sphere of the second coordination (metal-metal). This evolution is found in conformity with that resulting from the electronic structural analyses.

For the intermediate compositions of hexagonal type, the compounds most rich in arsenic are spontaneously ferromagnetic. On the other hand, for the compounds rich in phosphorus, the structure is antiferromagnetic.

The first order transition separating the two behaviours varies in temperature according to the selected composition. It is clear here that the strong magnetocaloric effect appears the most extremely ever detected there so far towards the ambient temperature. Our study made it possible to reveal that the magnetoelastic transition (magnetocaloric) had a base of the modifications in the coordination of iron, manganese remaining primarily with the identical one. In parallel iron undergoes, a marked evolution of its magnetic moment of $0.7 \mu_B$ approximately, the ferro one with the antiferromagnetism. The type of this last arrangement was identified like incommensurable magnetic structure at long period.

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