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Magneto-elastic properties of $MnFeP_{1-x}As_x$ ($0.15 \leq x \leq 0.66$) and $MnRhP_{1-x}As_x$ isostructural series of compounds

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Abstract

In both the series of ternary d-metal pnictides $MnFeP_{1-x}As_x$ and $MnRhP_{1-x}As_x$ the magnetic properties appear to be very sensitive to external parameters (temperature, pressure, magnetic field) and chemical composition. An extended analysis of previous experimental results is discussed in relation to the magneto-elastic phase transition in view of band structure calculations. The principal trends of these experiments are presented here. © 1997 Elsevier Science S.A.

Keywords: Magnetic phase transitions; Band structure calculations; High pressure measurements; Magnetisation measurements; Magnetic structures

1. Introduction

In this paper we present a short discussion of the crystal structure and magnetic properties of the $MnFeP_{1-x}As_x$ ($0.15 \leq x \leq 0.66$) and the $MnRhP_{1-x}As_x$ series in a wide range of compositions, temperatures, magnetic fields and external pressures.

The above mentioned systems belong to a large class of ternary MM'X (where M, M' is a transition element; X is a non-metal element) intermetallic compounds with unusual magnetic properties. The pnictides crystallise, almost exclusively, in a tetragonal (the Fe_2As-type, *P4/nmm*), hexagonal (the Fe_2P-type, $P\bar{6}2m$) or orthorhombic (the Co_2P type, *Pnma*) crystal structure. In the course of this work, only isostructural hexagonal series of compounds are considered where the most interesting magnetic properties are observed. The $MnFeP_{1-x}As_x$ ($0.15 \leq x \leq 0.66$) and the $MnRhP_{1-x}As_x$ series allow us to relate the crystal structure and magnetic properties of the material, which are marked functions of 3d metal atom distances [1–4].

The magnetic interactions between Mn–Mn, Mn–Fe, Fe–Fe and Mn–Rh atoms have been found to be strongly dependent on the corresponding interatomic distances. This is confirmed by the features of densities of states (DOS) calculated using the Korringa–Kohn–Rostoker method with the coherent potential approximation (KKR–CPA) [1].

2. Results and discussion

The magnetic (B, T) phase diagrams of the $MnFeP_{1-x}As_x$ system exhibit two types of critical points, i.e. a critical end point (CEP) found for several

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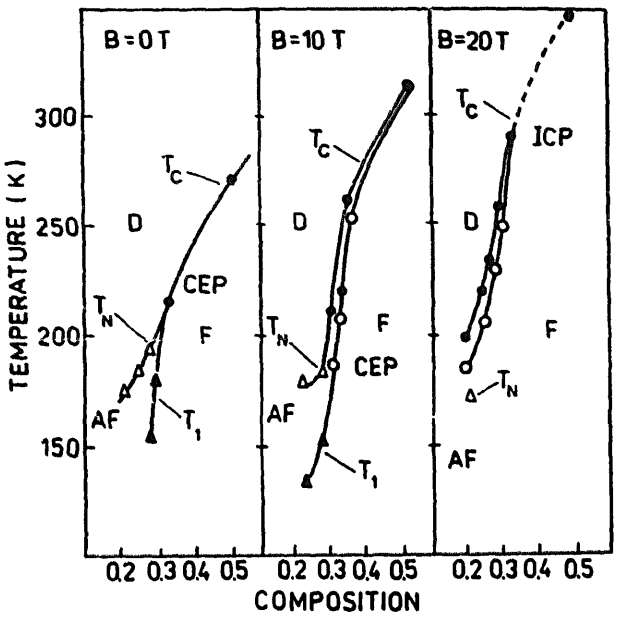

Fig. 1. (x, T)-magnetic phase diagrams of $MnFeP_{1-x}As_x$ determined under different magnetic fields ($B = 0$ T, $B = 10$ T and $B = 20$ T): AF, F and D represent long-range anti-ferromagnetic, ferromagnetic and disordered states, respectively; T_C and T_N are the Curie and Néel temperatures, respectively; T_1 is the AF–F phase transition temperature; CEP and ICP denote the critical end point and the isolated critical point, respectively [3].

compositions $0.2 \leq x \leq 0.275$ and a rare phenomenon in solid state, an isolated critical point (ICP) detected for $x = 0.33$ and $x = 0.5$ samples (Fig. 1). Assuming that changes in the magnetisation result both from changes in the interatomic distances and from the action of the external magnetic field, qualitative similarity between the (x, T) and (B, T) phase diagrams may be expected (as observed in Fig. 1). Thus, the long-range helimagnetic ordering in the $MnFeP_{1-x}As_x$ vanishes under a sufficiently strong magnetic field. The (B, T) phase diagram can be explained in the framework of the molecular field approximation [2,3] as well as in relation to the KKR–CPA results [3].

Neutron diffraction studies show that in the hexagonal domain of the $MnFeP_{1-x}As_x$ system both ferromagnetic and helimagnetic structures are observed [4]. In these two magnetic states the magnetic moments are localised on the Mn (3g) and on the Fe (3f) atoms. Magneto-elastic phase transitions observed in the $MnFeP_{1-x}As_x$ system can be associated with changes in the Mn–Fe and Fe–Fe distances as well as with changes in the density of states near the Fermi level, mainly due to the d-DOS on the Fe atoms [4]. For all the studied compositions of $MnFeP_{1-x}As_x$ series of compounds a short-range magnetic order occurs above the Curie or the Néel temperature [4].

In the case of the $MnRhP_{1-x}As_x$ system, several field-induced discontinuous phase transitions were evidenced [5]. The (B, T) phase diagrams reveal several critical points. However, the most interesting magnetic properties were found under external pressure in the $MnRhP_{0.5}As_{0.5}$ sample [6], namely the pressure-induced phase transition between the anti-ferromagnetic and ferromagnetic states was observed (Fig. 2). In the case of the $MnRhP_{1-x}As_x$ system the increase in phosphorus content and the application of external pressure lead to ferromagnetic ordering. As concluded from the KKR–CPA calculations, this behaviour can be related to modifications of the electronic states near the Fermi level on the Mn site. A unique mechanism was found to apply in the disordered $MnRhP_{1-x}As_x$ system with varying x and while changing the unit cell volume under pressure in the ordered MnRhP. Hence, the energy band shift near E_F vs. the rate of substitution x in the isoelectronic $MnRhP_{1-x}As_x$ may be interpreted in terms of a so-called 'chemical pressure' [1].

In Fig. 3 the dispersion curves $E(k)$ along the high

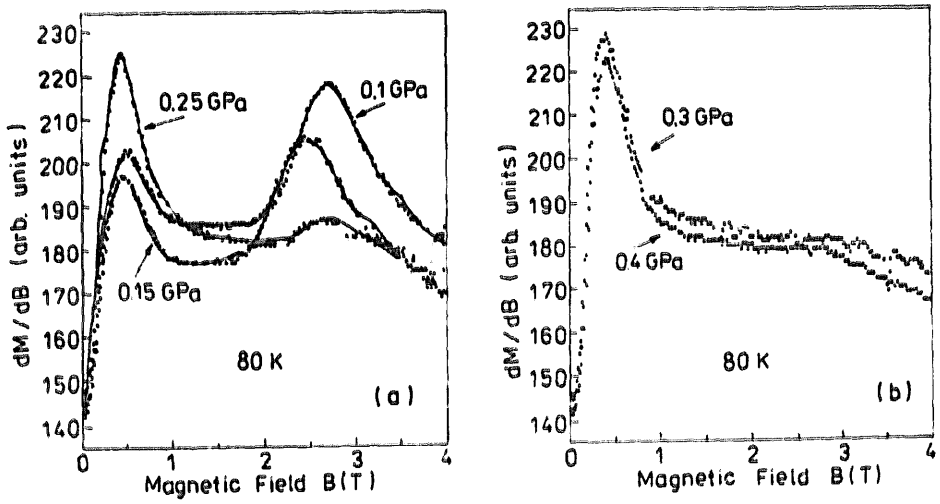

Fig. 2. Derivatives of magnetisation vs. magnetic field measured at 80 K for $MnRhP_{0.5}As_{0.5}$ at selected pressures: (a) $P < 0.3$ GPa; (b) $P \geq 0.3$ GPa.

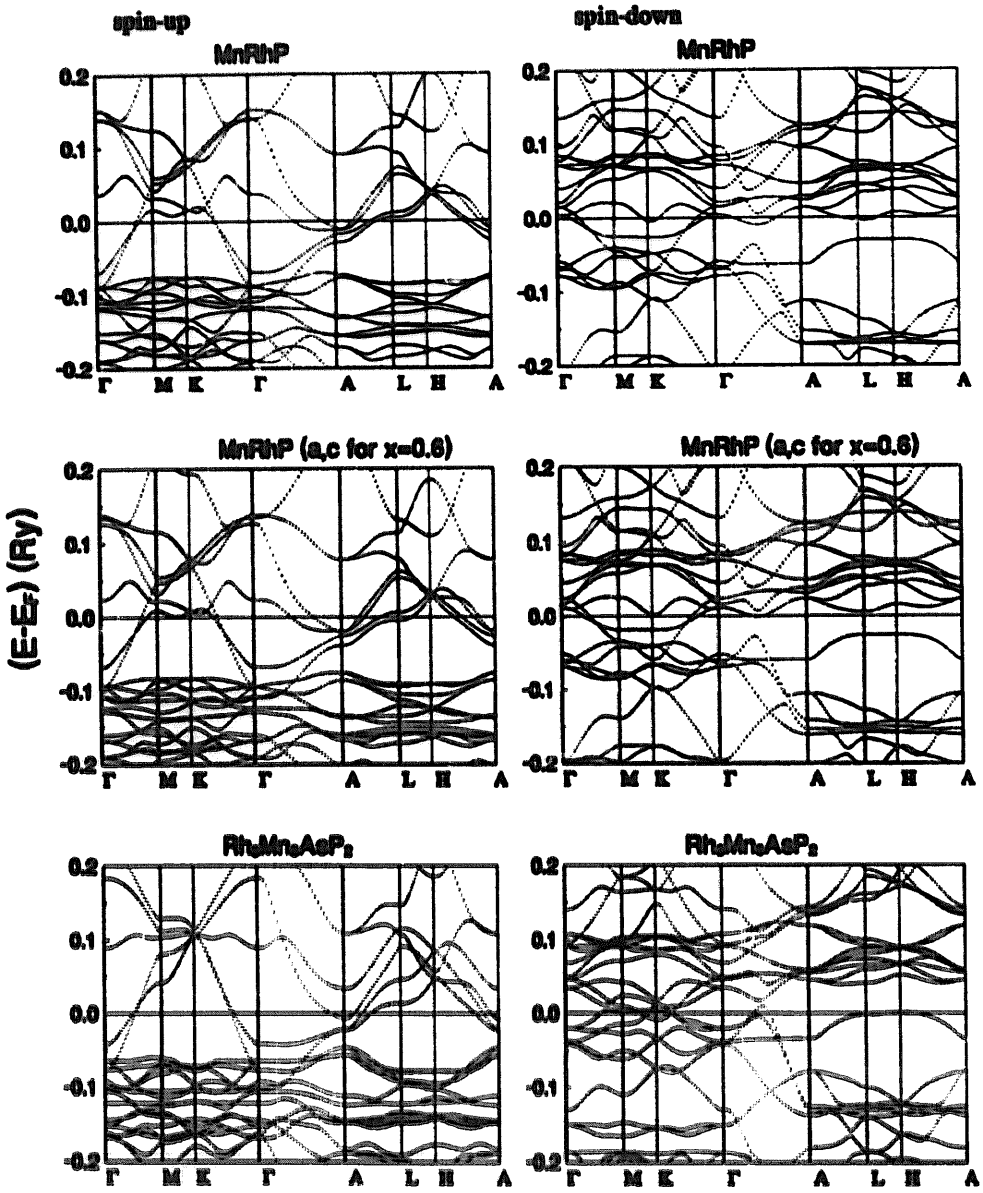

Fig. 3. The dispersion curves $E(k)$ along the high symmetry directions in the Brillouin zone for MnRhP, MnRhP-mod and hypothetical $Mn_3Rh_3P_2As$ compounds [1,3].

symmetry direction in the Brillouin zone are presented for MnRhP, MnRhP-mod (modified using the crystal data measured for $MnRhP_{0.6}As_{0.4}$) and hypothetical $Mn_3Rh_3P_2As$ (close to the disordered $MnRhP_{0.67}As_{0.33}$ alloy). Comparison with MnRhP, where the Fermi level lies at the sharp spin-down peak (bands are 'wrapped' around E_F), in MnRhP-mod and in $Mn_3Rh_3P_2As$ found that these bands are just above the Fermi energy. At the same time the spin-up bands do not change significantly, which affects the increase of the total magnetic moment per Wigner–Seitz cell from 9.02 μ_B in MnRhP to 9.94 μ_B in disordered $MnRhAsP_{0.6}As_{0.4}$ and 9.89 μ_B in MnRhP-mod, since the magnetic moment on Mn(3g) slightly increases from 3.07 μ_B to 3.38 μ_B and 3.31 μ_B, respectively. Table 1 presents the measured magnetic moments on Mn for MnRhP and MnRhAs parent compounds, which support the above-mentioned mechanism.

In both systems of solid solutions the magnetic moments of the Mn atoms exhibit an itinerant character. The local Stoner criterion for ferromagnetism is fulfilled both for the Mn and for the Fe atoms but not for the rhodium ones. Nevertheless, a significant density of states was pointed out near the Fermi level on the Rh site.

From the partial densities of states for the $MnFeP_{1-x}As_x$ system we can see that the Fermi level lies at the minimum of the d-DOS on Mn site, while the E_F is located on the sharp slope of the spin-down DOS on the Fe site.

Furthermore, as seen from the Table 1, there is a

Table 1
Theoretical and experimental values of the Mn, Fe and Rh magnetic moments and hyperfine fields in $MnFeP_{1-x}As_x$ and $MnRhP_{1-x}As_x$ systems

	Magnetic moment (μ_B)		Hyperfine field (T)	
	Measured	Calculated	Measured	Calculated
$MnFeP_{0.7}As_{0.3}$				
Mn	2.55 (0.2)	3.02	—	18.6
Fe	1.25 (0.2)	1.25	19.1	15.3
$MnFeP_{0.5}As_{0.5}$				
Mn	2.02 (0.3)	3.01	—	18.2
Fe	1.48 (0.3)	1.20	18.1	15.6
MnRhAs				
Mn	3.5 ÷ 3.6	3.42	—	—
Rh	0 ÷ 0.2	0.0	—	—
MnRhP				
Mn	3.13 (0.1)	3.07	—	—
Rh	0.02 (0.1)	0.0	—	—
$MnRhP_{0.8}As_{0.2}$				
Mn	3.14 (0.1)	3.2	—	—
Rh	—	0.0	—	—

good agreement between the band structure calculations and the experimental data (deduced from the neutron diffraction measurements and from the Mössbauer spectroscopy analysis). The magnetic moment of Mn is significantly stronger (approx. 3 μ_B) than that of Fe (approx. 1 μ_B). The Fe d-DOS, that give rise to weakly localised magnetic moments, are markedly modified at the magneto-elastic transition. It turns from 0.5 μ_B in the AF-long range to 1.2 μ_B in the ferromagnetic state. Thus, the magneto-elastic transition induced by changes of temperature, composition or external magnetic field may originate from features of the DOS on the Fe site.

A marked covalent character of the chemical bonds is present in both series of compounds. The DOS curves obtained for several As contents (with $x = 0.3$, $x = 0.33$ and $x = 0.5$ in the case of $MnFeP_{1-x}As_x$ system and with $x = 0$; $x = 0.4$; $x = 0.67$ and $x = 1$ in the case of the $MnRhP_{1-x}As_x$ system) indicate a strong s-, p- and d-hybridisation of the electron states [3].

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