Magnetostructural phase transitions in phosphor-containing manganese arsenide crystals

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Abstract. This article study investigates the magnetic and magnetocaloric properties of MnAs(P) pnictide compounds using first-principles calculations. In the $MnAs_{0.97}P_{0.03}$ solid solution, a significant decrease in magnetization was observed, corresponding to a transition from ferromagnetic to paramagnetic ordering. The magnetostructural phase transition responsible for this behavior induces a noticeable magnetocaloric effect near the critical temperature. To analyze these phenomena, the local density approximation with gradient corrections (LDA+GGA) was employed. The interatomic exchange integrals were evaluated by differentiating the total energy functional with respect to spin-pair deviations from equilibrium. The results reveal that increasing phosphorus concentration enhances the magnetic anisotropy within structural blocks, necessitating stronger external magnetic fields to achieve complete ferromagnetic alignment. These findings contribute to a deeper understanding of tunable magnetocaloric materials for solid-state refrigeration and magnetic energy conversion app.

Keywords: magnetocaloric effect, magnetostructural phase transition, ferromagnetic-paramagnetic transition, magnetization behavior; electronic structure; phosphorus substitution, crystal lattice parameters, spin-pair interactions.

1. Introduction

The development of compact, environmentally sustainable, and energy-efficient refrigeration systems operating near room temperature has become increasingly significant in recent years. This growing interest is primarily driven by global concerns about greenhouse gas emissions, the environmental impact of conventional vapor-compression refrigerants, and the need for alternative solid-state cooling technologies. Among the most promising approaches is magnetic refrigeration, which is based on the magnetocaloric effect (MCE) – a reversible change in temperature of magnetic materials under the influence of an applied magnetic field [1-2].

The MCE reaches its maximum near the region of magnetic phase transitions, particularly in materials exhibiting strong coupling between magnetic and structural degrees of freedom. Such magnetostructural transitions are characteristic of certain transition-metal-based alloys, notably

those containing elements from groups 5-7 of the periodic table [3-6]. These materials are of special interest because their first-order magnetostructural transformations can yield large entropy changes and high adiabatic temperature variations, which are desirable for high-performance magnetic refrigeration applications.

Despite significant progress, a comprehensive understanding of how minor chemical substitutions affect the magnetocaloric and magnetic properties of these compounds remains incomplete. In particular, elucidating the correlation between electronic structure, magnetic anisotropy, and phase transition behavior is essential for the rational design of tunable magnetocaloric materials. Therefore, this study focuses on analyzing the influence of phosphorus substitution in MnAs-based pnictides, aiming to clarify the mechanisms that govern their magnetic and magnetocaloric characteristics using first-principles calculations.

In this context, the investigation of the structural and magnetic properties of manganese-based pnictides, as well as their evolution with temperature and chemical substitution, remains of significant scientific interest. These compounds serve as model systems for studying the fundamental mechanisms of magnetostructural phase transitions, as they exhibit a wide variety of both first- and second-order transformations.

Previous studies have primarily focused on understanding the magnetocaloric effect in MnAs-based pnictides with partial substitution of manganese by transition metals [7-12]. Such investigations provided valuable insights into how electronic and magnetic interactions influence the entropy change and magnetization behavior near the critical temperature.

Building upon these earlier findings, the present work aims to analyze the influence of limited phosphorus substitution in the arsenic sublattice on the structural and magnetic phase transition characteristics of MnAs-based pnictide compounds. The goal is to elucidate how minor anionic substitutions modify the magnetostructural coupling and magnetic anisotropy, thereby affecting the overall magnetocaloric response of the system [36].

2. Materials and methods

Recently, perovskite manganites have been the subject of intensive research since they allow variation of the phase transition temperature over a wide range, thereby enabling a broader operational temperature interval for the magnetocaloric effect (MCE). In addition, these materials are economically viable and technologically accessible [1, 3]. Polycrystalline powders of solid solutions in the $MnAs_{1-\gamma}P_{\gamma}$ system were synthesized using the solid-state reaction method by melting the initial components in vacuum-sealed quartz ampoules within a single-zone resistance furnace [5, 9]. Specifically, $MnAs_{0.97}P_{0.03}$ and $MnAs_{0.95}P_{0.05}$ samples were synthesized. The synthesis procedure followed established techniques for preparing manganese pnictides [9, 12]. Finely dispersed powders of manganese, phosphorus, and arsenic were mixed in stoichiometric ratios and sealed in evacuated quartz ampoules for the reaction.

The phase composition and unit cell parameters at room temperature were determined by X-ray diffraction (XRD) analysis using CuKα radiation. The isothermal entropy change associated with the phase transition was determined from magnetization measurements carried out in static magnetic fields up to 14 T [4], employing a vibrating sample magnetometer (Cryogenic Limited). Magnetocaloric properties were subsequently calculated indirectly using the Maxwell thermodynamic relation [10].

3. Results and discussion

Previous studies [15, 16] based on measurements of structural parameters, magnetic susceptibility, elastic, and other physical properties of equiatomic MnAs have demonstrated that a first-order magnetostructural phase transition occurs upon heating above 316 K. At this temperature, manganese arsenide undergoes a transformation from a ferromagnetic phase with a hexagonal crystal structure of the B81 type to a paramagnetic phase with an orthorhombic crystal

structure of the B31 type.

According to X-ray diffraction (XRD) analysis, $MnAs_{1-\gamma}P_{\gamma}$ compounds with phosphorus concentrations below $y = 0.05$ crystallize as single-phase materials adopting the orthorhombic B31 structure. The calculated lattice parameters (a, b, c), the axial ratio (c/a), and the unit cell volume (V) for these solid solutions are summarized in Table 1

Table 1. Parameters a, b, and c, and unit cell volume V of the $MnAs_{1-\gamma}P_{\gamma}$ solid solutions

x	a, nm	b, nm	c, nm	V, 10^{-2} nm^3
0,03	0,5678	0,3627	0,6316	7,791

Calculations of the electronic structure and interatomic exchange integrals were performed using the fully relativistic Korringa-Kohn-Rostoker (KKR) method implemented in the SPR-KKR package (version 8.6) [10]. The simulations were conducted within the framework of the Coherent Potential Approximation (KKR-CPA) to properly account for the effects of chemical disorder in the alloys. The Atomic Sphere Approximation (ASA) was employed to describe the crystal potential.

For the exchange-correlation energy, the Local Density Approximation (LDA) with gradient corrections was adopted, as it provides the best correspondence between the calculated magnetic moments and the available experimental data [10, 22]. The interatomic exchange integrals were determined using the formalism described in [10, 23], which evaluates the variation of the total energy functional with respect to small deviations of specific spin pairs from their equilibrium orientations.

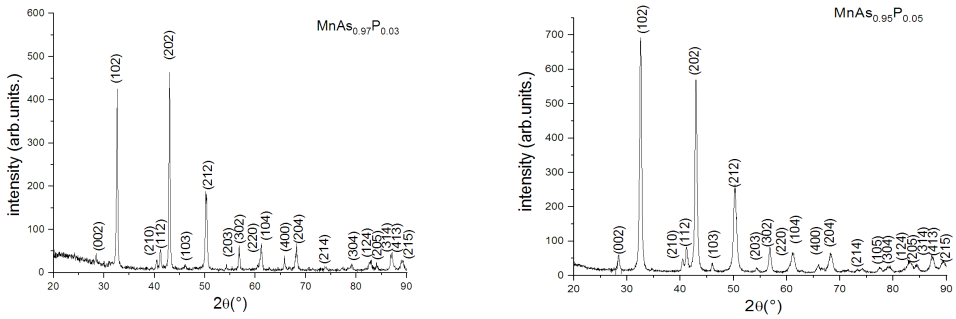

Fig. 1. X-ray diffraction patterns of $MnAs_{0.97}P_{0.03}$ and $MnAs_{0.95}P_{0.05}$ pnictides

The interatomic exchange interactions and the corresponding electronic structure were evaluated using the fully relativistic Korringa-Kohn-Rostoker (KKR) approach, as implemented in the SPR-KKR package (v8.6) [10, 18]. The computations were performed within the Coherent Potential Approximation (KKR-CPA) to accurately describe the effects of compositional disorder in the alloy system, while the crystal potential was modeled using the Atomic Sphere Approximation (ASA). For the exchange-correlation energy, the Local Density Approximation (LDA) with gradient corrections [10, 20] was applied, as it provided the best consistency between the calculated magnetic moments and experimental results. The interatomic exchange parameters were subsequently determined according to the methodology proposed in [10, 22], which evaluates the variation of the total energy functional in response to infinitesimal deviations of specific spin pairs from their equilibrium orientations.

The calculated electronic density of states (DOS) for $MnAs_{0.97}P_{0.03}$ and $MnAs_{0.95}P_{0.05}$ is presented in Fig. 2. The spin-resolved DOS spectra display a pronounced multi-peak structure, which is typical for pnictide compounds containing 3 d transition metals [10]. The observed features reflect the hybridization between the Mn 3 d and As(P) p states, indicating strong spin-dependent interactions that govern the magnetic behavior of the solid solution.

The substitution of arsenic atoms with phosphorus, while maintaining constant crystal lattice

parameters, results in a slight upward shift of the Fermi level. Despite this modification, the local magnetic moment of manganese atoms remains practically unchanged at 3.3 μB. Similarly, the interatomic exchange integrals exhibit only minor sensitivity to the As→P substitution, indicating that phosphorus incorporation does not significantly alter the overall exchange coupling mechanism (Fig. 3).

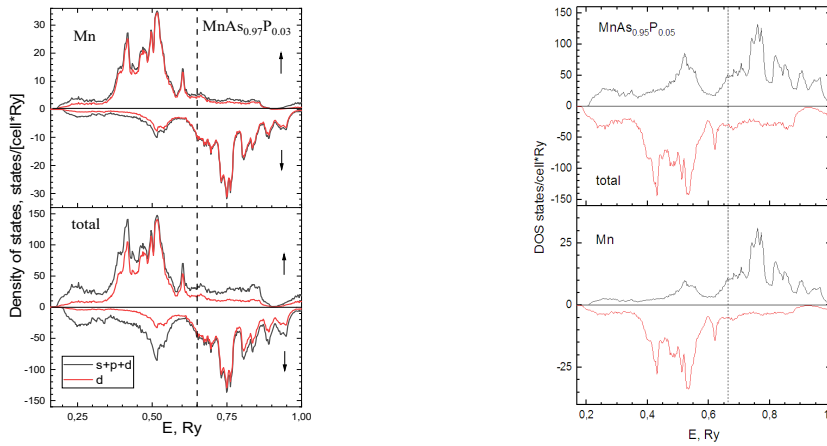

Fig. 2. Electronic density of states of $MnAs_{0.97}P_{0.03}$ and $MnAs_{0.95}P_{0.05}$ pnictides. The Fermi level position is indicated by a vertical line

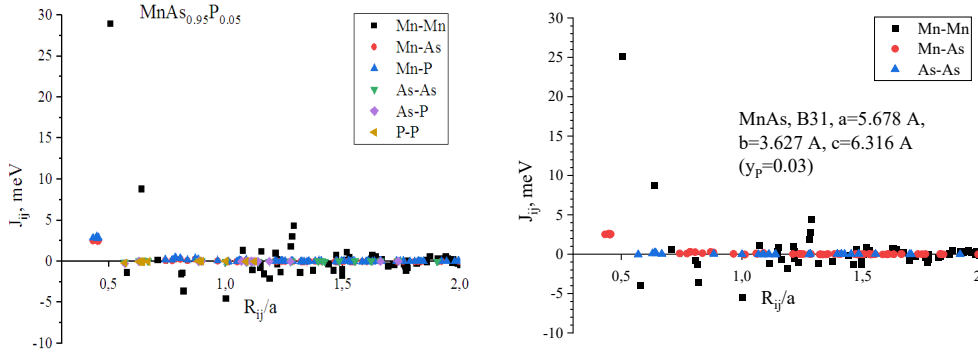

Fig. 3. Dependence of interatomic exchange integrals on distance in $MnAs_{0.95}P_{0.05}$ and in pure MnAs with the lattice parameters of $MnAs_{0.95}P_{0.05}$

4. Conclusions

The results of field-dependent magnetization measurements for the $MnAs_{0.95}P_{0.05}$ sample, conducted in magnetic fields up to 14 T, are shown in Fig. 4. The data reveal a partial restoration of the ferromagnetic phase within the temperature range of approximately 240-320 K, occurring when the applied magnetic field exceeds a critical value (H_k). Notably, this critical field increases substantially beyond 14 T, indicating the stabilization of ferromagnetic ordering under strong external magnetic fields.

The calculated temperature dependence of the magnetic entropy change (ΔS_m) for the $MnAs_{0.97}P_{0.03}$ composition revealed a maximum value of approximately 61 $J \cdot kg^{-1} \cdot K^{-1}$ near 260 K, corresponding to a magnetic field variation from 0 to 14 T [10]. This pronounced peak in ΔS_m indicates a strong magnetocaloric response in the vicinity of the magnetostructural phase transition, confirming the significant coupling between magnetic and structural degrees of

freedom in the system.

It was established that increasing the phosphorus concentration leads to a linear decrease in the lattice parameters. The observed reductions in the a, b, and c parameters can be attributed to the difference in the ionic radii of arsenic and phosphorus atoms. At temperatures above 280 K, the application of a magnetic field of $H = 14$ T results in the re-establishment of the ordered ferromagnetic state, which occurs through the reorientation of crystallite magnetization vectors parallel to the external field [14]. As a consequence, the hexagonal B81 phase re-emerges, displaying its characteristic ferromagnetic ordering. The partial substitution of phosphorus enhances the magnetic anisotropy of individual structural blocks, thereby requiring stronger external magnetic fields to stabilize the ferromagnetic phase compared to equiatomic MnAs [14].

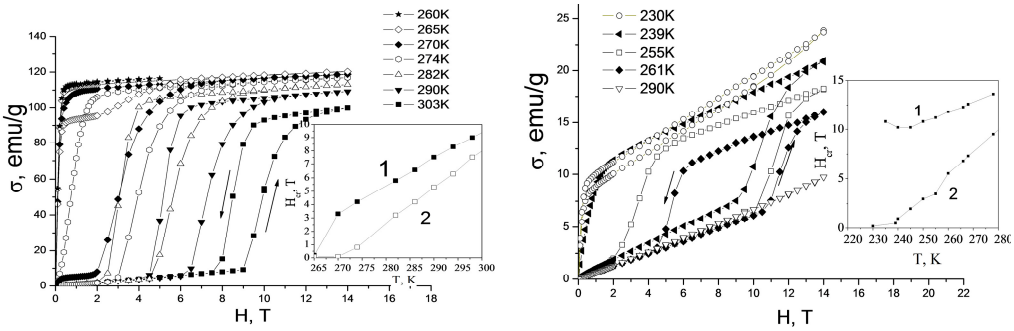

Fig. 4. a) Field-dependent magnetization curves of the $MnAs_{0.97}P_{0.03}$ sample recorded during heating and cooling in the vicinity of the phase transition temperature. Inset: temperature dependence of the critical magnetic field H_k, corresponding to the transition from the ferromagnetic ordered state to the disordered state (curve 1) and to the reverse transition (curve 2), b) field dependencies of the magnetization of $MnAs_{0.95}P_{0.05}$ pnictide near the phase transition temperature. Inset: temperature dependence of the critical magnetic field H_k for the transition from a partially ordered ferromagnetic state to a disordered one – curve 1, and for the reverse transition – curve 2

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Data availability

The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

Conflict of interest

The authors declare that they have no conflict of interest.

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