ISSN 0031-918X, Physics of Metals and Metallography, 2025, Vol. 126, No. 9, pp. 1017–1021. © Pleiades Publishing, Ltd., 2025.

ELECTRICAL AND MAGNETIC PROPERTIES

Magnetic and Magnetocaloric Characteristics of Mixed Manganese Pnictides

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Received June 18, 2025; revised July 17, 2025; accepted July 29, 2025

Abstract—Substituted $MnAs_{0.97}P_{0.03}$ manganese arsenide is prepared, and its structural, magnetic, and magnetocaloric properties are studied. At ~260 K, an abrupt decrease in the magnetization of the sample is observed, which is interpreted as a ferromagnetic–paramagnetic transition. The magnetostructural phase transition is accompanied by the magnetocaloric effect, which is observed in magnetic fields up to 13.5 T.

Keywords: magnetocaloric effect, phase transition, electronic structure

DOI: 10.1134/S0031918X25601040

INTRODUCTION

In recent years, interest in investigations into the magnetocaloric effect (MCE) is driven by the industrial need for materials required for creating magnetic refrigerators, in which such materials can act as the working body [1–3]. This will eliminate the use of environmentally harmful refrigerants. Cost-effective materials exhibiting a giant MCE observed at room temperature are of greatest interest. They include materials with first-order magnetostructural phase transitions, in particular, some alloys of transition metals with elements of groups V–VII [4–9]. The first-order magnetostructural phase transitions are characterized by distortion of the crystal lattice and the release of transition heat [10–16]. In this regard, the study of structural and magnetic characteristics and their changes with temperature, pressure, alloying in the transition region, and the determination of the transition heat in the magnetostructural phase transition region are of importance for understanding the causes and mechanisms of their occurrence [17, 18].

Manganese pnictides, being kind of model objects for studying the nature of the magnetostructural phase transition, are one of interesting materials, in which a whole range of both first- and second-order magnetic and structural phase transformations occur. Earlier, in order to establish the mechanisms for the appearance of the MCE upon such transitions, we studied pnictides with the partial substitution of transition metals atoms for manganese atoms [19–24].

The aim of this study is to investigate the influence of small substitutions in the arsenic sublattice on the magnetostructural phase transitions of the MnAs polycrystalline compound. Phosphorus was chosen as the alloying element, since its outer electron shell is identical to that of As. However, the atomic radius of phosphorus is smaller; this allows the influence of external hydrostatic pressure to be simulated by the substitution of phosphorus atoms for arsenic atoms [25, 26].

EXPERIMENTAL

At the first stage of the study, the $MnAs_{0.97}P_{0.03}$ sample was prepared by solid-phase synthesis [19]. Fine manganese, phosphorus, and arsenic powders were taken in appropriate proportions and placed in evacuated quartz ampoules and annealed at 1073 K for 7 days.

The phase composition and crystal lattice parameters were determined by X-ray diffraction analysis performed at room temperature using a DRON-3M diffractometer and Cu$K\alpha$ radiation.

† Deceased.

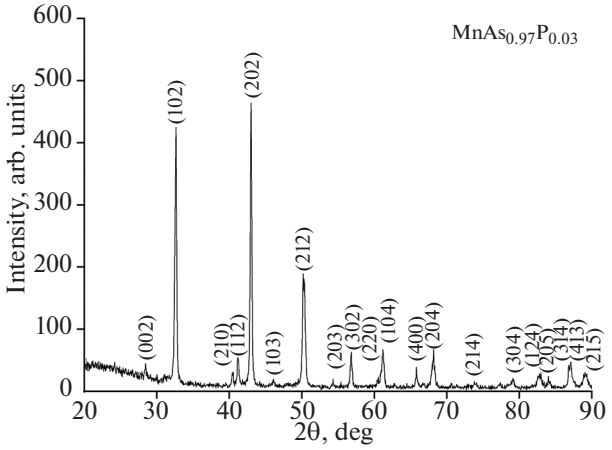

Fig. 1. X-ray diffraction pattern of $MnAs_{0.97}P_{0.03}$.

To determine the isothermal entropy change near the phase transition, the magnetization was measured in static fields up to 13.5 T. A vibrating sample magnetometer (VSM) (Cryogenic Limited) was used. Magnetocaloric characteristics were calculated indirectly using the Maxwell's thermodynamic relationship.

RESULTS AND DISCUSSION

Previously [27, 28], based on measurements of structural parameters, magnetic susceptibility, elastic, and other physical properties of the equiatomic MnAs composition, the first-order magnetostructural phase transition is shown to occur upon heating above 316 K. When the temperature increases above 316 K, the manganese arsenide transfers from the ferromagnetic phase with the $B8_1$ hexagonal crystal lattice to the paramagnetic phase with the $B31$ rhombic crystal lattice. Neutron diffraction data [29, 30] also showed that this phase transition at the T_C temperature is classified among order–disorder magnetic $B8_1$–$B31$ transitions with changing the symmetry, whereas the phase transition at the higher temperature, $T_K \sim 380$ K, is the reverse $B31$–$B8_1$ transition.

The X-ray diffraction analysis (Fig. 1) showed that the $MnAs_{0.97}P_{0.03}$ sample at room temperature has the $B31$ structure (space group *Pnma*); the crystal lattice parameters are given in Table 1. Small substitutions of phosphorus for arsenic are shown to lead to the decrease in the crystal lattice parameters as compared to that of the equiatomic composition.

The doping of MnAs with phosphorus results in changes in the crystal lattice parameters, i.e., it is equivalent to a "chemical pressure" [25, 26].

Table 1. Crystal lattice parameters of the $MnAs_{0.97}P_{0.03}$ and equiatomic MnAs compounds

Sample	a, Å	b, Å	c, Å
$MnAs_{0.97}P_{0.03}$	5.678	3.627	6.316
MnAs [34]	5.695	3.644	6.329

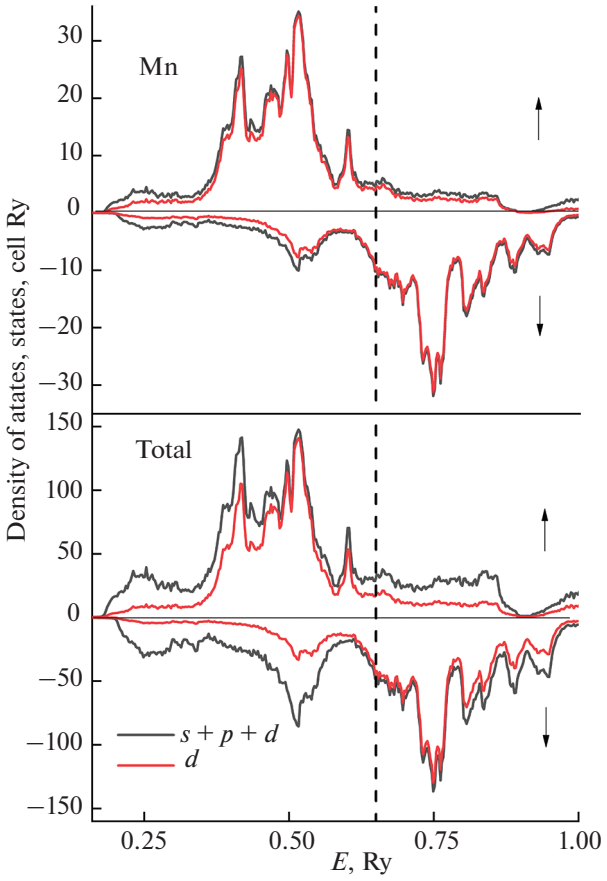

Fig. 2. Density of electron states of $MnAs_{0.97}P_{0.03}$. Position of the Fermi level is shown with a vertical line.

The electronic structure and interatomic exchange integrals were calculated using the fully relativistic Korringa–Kohn–Rostoker method (SPRKKR v8.6 package [31]) and coherent potential approximation (KKR-CPA) for a disordered alloy. The atomic-sphere approximation was used for the calculation of crystal potential. For the exchange-correlation energy, the approximation, which provides the best agreement between the calculated magnetic moments and experimental values, was chosen. The local density approximation [32] taking into account gradient corrections was used. Interatomic exchange integrals were calculated using a procedure available in [33], which is based on the calculation of the variation of total energy functional based on the deviation of a selected spin pair from the equilibrium position. For the calculations, we used literature data for the parameters of positions occupied with Mn and As atoms; the positions are 4*c* (x, 1/4, z) with parameters $x_{Mn} = 0.0045$, $z_{Mn} = 0.2160$, $x_{As} = 0.2196$, $z_{As} = 0.5774$ [34].

Figure 2 shows the electron density of states for $MnAs_{0.97}P_{0.03}$.

The spin-polarized density of electron states has a multi-peak structure typical of 3*d*-metal compounds

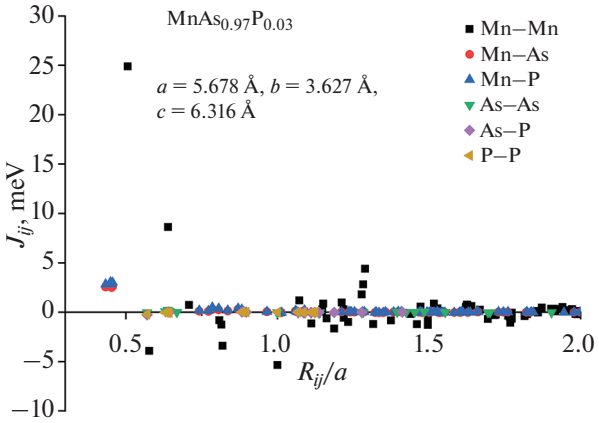

Fig. 3. Dependence of interatomic exchange integrals on the interatomic spacing for $MnAs_{0.97}P_{0.03}$.

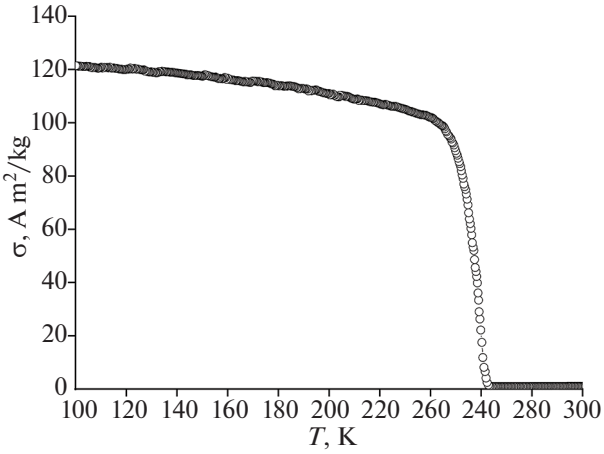

Fig. 4. Temperature dependence of the magnetization measured during cooling of the $MnAs_{0.97}P_{0.03}$ sample in a magnetic field of 1 T.

[24]. The substitution of phosphorus atoms for 3% of arsenic atoms, while maintaining the crystal lattice parameters, results in a slight increase in the Fermi level. The local magnetic moment of Mn remains unchanged (3.3 μ_B). Figure 3 shows the dependence of the effective exchange integrals for $MnAs_{0.97}P_{0.03}$ on the interatomic spacing. The main contribution to the formation of the magnetic structure is made by the exchange interaction between the nearest manganese atoms located in the basal plane $J_1 = 24.9$ meV. The Mn–Mn exchange interaction in the second coordination sphere is negative $J_2 = -3.9$ meV. The Mn–As and Mn–P exchange interactions do not exceed 3 meV. The Curie temperature of $MnAs_{0.97}P_{0.03}$, which was calculated based on exchange interactions in the molecular field approximation, is 376 K.

Figures 4 and 5 shows the temperature dependences of the magnetization of $MnAs_{0.97}P_{0.03}$ measured in fields up to 13.5 T.

It follows from the presented data that, above the phase transition temperature of ~260 K, the ferromagnetic state of the $MnAs_{0.97}P_{0.03}$ pnictide is restored when the magnetic field exceeds a certain critical value.

As is known [20], as the phosphorus content increases in the $MnAs_{0.99}P_{0.01}$ and $MnAs_{0.98}P_{0.02}$ compositions, the temperature of the first-order phase transition decreases as compared to that of the equiatomic composition, which also correlates for the $MnAs_{0.97}P_{0.03}$ composition.

The magnetic entropy change of the studied sample was determined using a set of isothermal magnetization curves and Maxwell's relation:

$$\frac{\partial S}{\partial B} = \frac{\partial M}{\partial T}. \quad (1)$$

Figure 6 shows the temperature dependence of the magnetic entropy change for $MnAs_{0.97}P_{0.03}$, which was determined using the Maxwell's relation.

When the isothermal magnetization of the sample is fulfilled at a temperature of 274 K, which induces the ferromagnetic state, the phase transition is completely occurs in a magnetic field of ~6 T. Also, it is seen that the increase in the temperature above the transition temperature leads to a decrease in hysteresis, which is inherent for substances of this class [10].

The performed studies allowed us to find that, when the magnetic field changes from 0 to 13.5 T, the maximum magnetic entropy change for $MnAs_{0.97}P_{0.03}$ is ~61 J/(kg K) and is observed at a temperature of ~268 K. At temperatures above 260 K, the external magnetic field destroys the paramagnetic orthorhombic phase and causes the magnetostructural transition with the formation of the hexagonal phase. The existence of the complex magnetostructural transition near

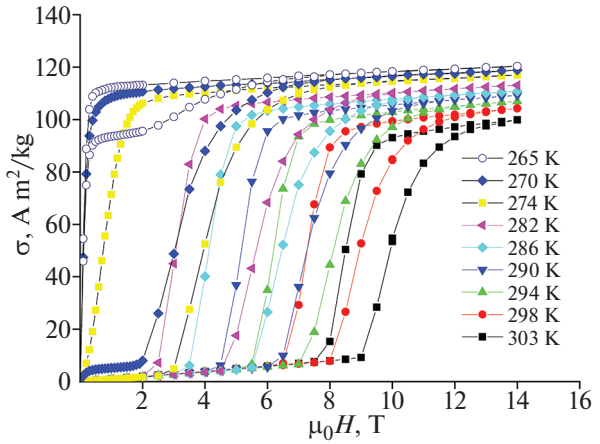

Fig. 5. Field dependences of the magnetization of $MnAs_{0.97}P_{0.03}$ near the phase transition temperature.

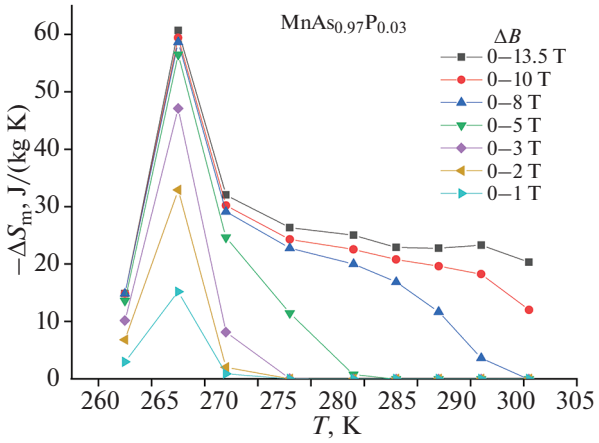

Fig. 6. Temperature dependences of the isothermal magnetic entropy change ΔS_m for $MnAs_{0.97}P_{0.03}$ measured in different magnetic fields.

~260 K leads to the formation of non-uniform magnetostructural state with the formation of ferro- and paramagnetic domains, within which either the hexagonal crystal lattice with the ferromagnetic order or the orthorhombic crystal lattice with the paramagnetic state forms.

CONCLUSIONS

Experimental studies of the magnetic properties and calculations of the density of states of the $MnAs_{0.97}P_{0.03}$ pnictide were carried out.

Magnetic measurements showed the presence of the magnetostructural phase transition, which leads to the appearance of the MCE. It is shown that, as magnetic field changes from 0 to 13.5 T, the maximum magnetic entropy change is ~61 J/(kg K) at a temperature of ~260 K.

The spin-polarized density of electron states is shown to have the multi-peak structure typical of 3*d*-metal compounds. Doping of the MnAs pnictide with phosphorus results in changing the crystal lattice parameters, i.e., is equivalent to a "chemical pressure."

FUNDING

The study was supported by the Belarusian Republican Foundation for Fundamental Research, project no. T25UZB-053.

CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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Translated by N. Kolchugina

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