Magnetic field induced order–order phase transition in magnetocaloric systems Mn$_{2-x}$Fe$_x$As$_{0.5}$P$_{0.5}$ and MnFeAs$_y$P$_{1-y}$

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ABSTRACT

An analysis is presented of experimental and theoretical results of the MnFeAs$_y$P$_{1-y}$ ($0.15 \leq y \leq 0.66$) and Mn$_{2-x}$Fe$_x$As$_{0.5}$P$_{0.5}$ ($0.5 \leq x \leq 1.0$) systems to identify main traits that underlie the mechanism of formation of different antiferromagnetic (AF) phases in the two systems. The discrepancy between the calculated from first principles and experimental values of the magnetic moment in the ferromagnetic phase with cation substitution in the system Mn$_{2-x}$Fe$_x$As$_{0.5}$P$_{0.5}$ is due to the appearance of a canted magnetic structure. In this case, the emergence of an AF phase with decreasing iron concentration precedes a significant change in the electronic d-band filling. In the model of the spiral structure in the system of itinerant electrons it is shown that the stabilization of the AF phase with decreasing arsenic concentration, while maintaining the number of d-electrons, is a consequence of changes in the shape of the density of electronic states that occur with a decrease in unit-cell volume.

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1. Introduction

The advent of the NdFeB permanent magnets of special configurations able to produce magnetic field strength up to 2 T [1] and the revealing of giant magnetocaloric effect due to the presence of the first-order phase transition [2,3] stimulated discussion of potential of new types of refrigerators. In this case, heat is removed by a magnetocaloric device with the temperature reduced as a result of the first-order phase transition from the ferromagnetic (FM) state to the low magnetic (paramagnetic etc.) one. The transition occurs under cyclic decrease of magnetic field strength. As, in this case, the temperature cannot be decreased by more than five degrees [4], the cooling occurs in stages using a series of working materials with the time-spaced spontaneous magnetic disorder–order or order–order phase transitions.

The idea of development of such magnetic refrigerators stimulated studies of magnetocaloric phenomena in well-known and new materials and resulted in a great number of researches done all over the world. These works can be divided into two groups: i) studies of magnetocaloric properties of materials only, and ii) comprehensive investigations of the totality of magnetic properties of these subjects. The second direction is determined by fundamental characteristics of formation of magnetocaloric effects in materials with different types of magnetic phase transitions. This is absolutely evident that under the magnetic-field-induced first-order disorder–order phase transitions, discontinuous adiabatic magnetization (demagnetization) of the sample is accompanied by sudden decrease (increase) in the entropy and, as a consequence, by increase (decrease) of the temperature. The nature of the giant magnetocaloric effect in magnetic-field-induced order–order phase transitions is less transparent, since the change of magnetic entropy in the transitions changing only the type of magnetic order may be small. Then, the existence of magnetocaloric effect is determined by an additional contribution to the entropy change made by the magnetoelastic interaction [5] or by highly different degree of disorder in magnetic phases [6]. Many compounds demonstrate magnetic phase transitions of both types accompanied by a giant magnetocaloric effect. The most prospective is the series of the iron–manganese pnictides Mn$_{2-x}$Fe$_x$As$_y$P$_{1-y}$ with hexagonal crystal structure.

This paper is devoted to the analysis of differences in the formation of spontaneous and magnetic-field-induced magnetically ordered states in systems with the anion MnFeAs$_y$P$_{1-y}$ and cation Mn$_{2-x}$Fe$_x$As$_{0.5}$P$_0$ substitutions that are based on ab $initio$ calculation of the spin-polarized electron structure and on model approach.

2. Phase diagram and structure of magnetic phases of the Mn$_{2-x}$Fe$_x$As$_y$P$_{1-y}$ system

The temperature–concentration magnetic phase diagrams of systems with anion (MnFeAs$_y$P$_{1-y}$ [7]) and cation (Mn$_{2-x}$Fe$_x$As$_{0.5}$P$_{0.5}$ [8])

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substitutions presented in Fig. 1 demonstrate no qualitative difference in the formation of antiferromagnetic state to the left of the common point $x=1$, $y=0.5$ corresponding to the ferromagnetic phase. M.Bacmann et al. [9] determined magnetic structures by neutron diffraction methods for the case of anion substitution in the $MnFeAs_yP_{1-y}$ system. In the ferromagnetic phase, the magnetic moments of manganese and iron atoms are directed along the hexagonal axis c. Their magnitudes are $M(Mn)=2.6–2.9$ μ_B, $M(Fe)=1.0–1.5$ μ_B, depending on y. In the antiferromagnetic phase, a complex magnetic structure with the propagation vector $\vec{Q}=(2\pi/a)\,[0,q_y,0]$ is observed. The value of q_y varies from 0.293 to 0.35 depending on the temperature and the composition. The magnetic moments of manganese atoms in pyramidal positions (3 G) are located in a–c plane normal to the vector of structure propagation $\vec{b}^*$ and form a helical spiral with $M(Mn)=2.41$ μ_B. The magnetic moments of iron atoms in tetrahedral positions (3b) are directed along the hexagonal axis c and form the sinusoidal spin-density wave with amplitude $M(Fe)_{ampl}=0.43$ μ_B, which is less than a half of $M(Fe)$ in ferromagnetic phase.

As in the $Mn_{2-x}Fe_xAs_{0.5}P_{0.5}$ ($x < 0.6$) system, the crystal lattice structure is preserved, and it can be assumed that the antiferromagnetic state has a similar structure. On the other hand, one can state that the antiferromagnetic states of the $MnFeAs_yP_{1-y}$ and $Mn_{2-x}Fe_xAs_{0.5}P_{0.5}$ systems essentially differ as seen under strong magnetic field application.

For example, in the system with anion substitution, in antiferromagnetic samples of $MnFeAs_{0.25}P_{0.75}$, and $MnFeAs_{0.26}P_{0.74}$, the ferromagnetic phase becomes stable under increasing magnetic-field strength as a result of irreversible magnetic-field-induced first-order AF–FM transition, as shown in (Fig. 2a). (In the H–T diagrams [10,11], a similar transition is characterized by the finite value of the critical field for ferromagnetic phase advent ($H_{k1}(T) > 0$) in the whole temperature range as well as the FM phase vanishing field H_{k2} for $T < T_{12}=100$ K).) In this case, for the strong magnetic-field-induced state, the saturation magnetization (M_{exp} for $y=0.25–0.26$ in Fig. 2(a) exceeds that of the spontaneous FM state ($y=0.5$, $y=0.3$). In this compound, the antiferromagnetic phase can also be stable for $T < T_N$ in the case when the sample temperature initially decreases in fields lower than the first critical field $H_{k1} \approx 4$ T.

In antiferromagnetic compounds $Mn_{1.45}Fe_{0.55}As_{0.5}P_{0.5}$ and $Mn_{1.5}Fe_{0.5}As_{0.5}P_{0.5}$ (Fig. 2b), the magnetic-field-induced AF–FM transitions are reversible ($H_{k1} > 0$, $H_{k2} > 0$). Here, the saturation magnetization of the induced phase (as seen in Fig. 2b) is almost a half of the maximum value of saturation magnetization of FM state, which is spontaneous in the $Mn_{1.2}Fe_{0.8}As_{0.5}P_{0.5}$ sample [6,12].

To analyze the cause of qualitative differences in basic characteristics of systems with the anion substitution ($MnFeAs_yP_{1-y}$) and cation one ($Mn_{2-x}Fe_xAs_{0.5}P_{0.5}$), we have calculated the spin-polarized electronic structure of both systems.

3. Computational details and electronic structure

The spin-polarized electronic structure of the $Mn_{2-x}Fe_xAs_{1-y}P_y$ alloys was analyzed by fully relativistic spin-polarized Korringa–Kohn–Rostoker method (SPRKKR [13]). The crystal lattice potential was constructed within the atomic sphere approximation. The exchange-correlation energy was calculated within the local density approximation [14].

The $Mn_{2-x}Fe_xAs_{1-y}P_y$ alloys have the hexagonal Fe_2P crystal structure (the symmetry group is $P\bar{6}2m-D_{3h}^3$) [9,15]. For $x \le 1$, the Fe and Mn_I atoms occupy mainly positions with the tetrahedral ($I \equiv 3f$, ($x(3f),0,0$)) environment, Mn_{II} –is associated with pyramidal ($II \equiv 3g$, ($x(3g),0,1/2$)) arsenic and phosphorus atom environment where the atoms are assumed to be randomly distributed at $2c(1/3,2/3,0)$ and $1b(0,0,1/2)$ positions. In this way, the unit cell contains three formula units. For the ferromagnetic state, the electronic structure of alloys was calculated within the coherent potential approximation for the model of a disordered alloy at tetrahedral positions, and atoms of As and P are randomly distributed at $2c$ and $1b$ positions. The parameters of crystallographic positions for iron and manganese atoms are $x(3f)=0.257$, and $x(3g)=0.580$ respectively [17].

Crystal lattice parameters are taken from [10] for the $MnFeAs_yP_{1-y}$ system at the temperature of 130 K and for the $Mn_{2-x}Fe_xAs_{0.5}P_{0.5}$ system at room temperature [16].

The electronic structure of the $MnFeAs_yP_{1-y}$ alloys is typical for transition metal pnictides, and it is weakly composition dependent. To illustrate, we show the total and partial densities of electronic states for $MnFeAs_{0.25}P_{0.75}$ in ferromagnetic state (Fig. 3). There is an s-band of As and P in the vicinity of $E \approx 0$ Ry in the spectrum of occupied states. The conduction band is above $E=0.25$ Ry, and it is of the mixed character, formed by s-, p-states of As and P and by 3d-states of Mn and Fe. This fact is an evidence
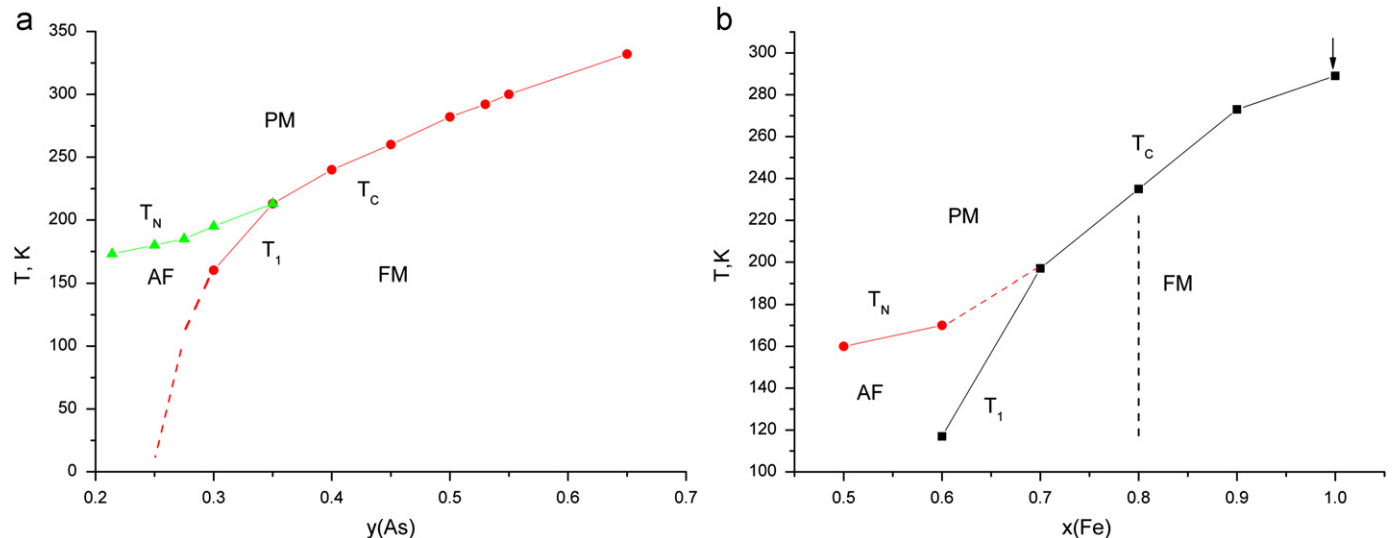

Fig. 1. Magnetic phase diagrams of the $MnFeAs_yP_{1-y}$ (a) [6] and $Mn_{2-x}Fe_xAs_{0.5}P_{0.5}$ (b) [7]. T_C is Curie temperature, T_N is Neel temperature, and T_1 is the temperature of order–order (FM–AF) phase transitions.