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ELECTRICAL AND MAGNETIC PROPERTIES

Magnetocaloric Effect of Zn-Containing Manganese Pnyctides

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Abstract—Magnetic and magnetocaloric characteristics of the $Mn_{1.9}Zn_{0.1}Sb$ and $Mn_{1.96}Zn_{0.04}Sb$ alloys are studied. The relatively abrupt decrease in the specific magnetization near 100 K is found, which, according to first-principals calculations, is interpreted as the antiferromagnet–ferrimagnet transition. The existence of the magnetic phase transition from the ferrimagnetic to antiferromagnetic state leads to the appearance of inverse magnetocaloric effect which remains in magnetic field up to 8 T.

Keywords: magnetocaloric effect, phase transition, electron structure

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INTRODUCTION

Manganese pnyctides are classified among advanced magnetocaloric materials, the application of which will allow one to simplify the construction of magnetic refrigerators and to decrease heat losses [1]. This is due to the existence of a great number of magnetic phase transitions in these compounds and relatively high parameters of inverse magnetocaloric effect [2]. The design of cryogenic magnetic refrigerators based on superconducting solenoids can be simplified at the expense of the fact that a magnetocaloric body during its magnetization in the course introduction of the body into the center of magnet will decrease the own temperature without heating surrounding structural elements [3–5]. Such a result occurs owing to the existence of inverse magnetocaloric effect in the material, whereas the direct magnetocaloric effect decreases the material temperature only during its demagnetization [6].

The $Mn_{2-x}Zn_xSb$ materials, for which the order–order transition is observed near 100 K [7–9], seem to be practical and useful. The aim of the present work is to study the structural, magnetic, and magnetocaloric characteristics of the $Mn_{1.9}Zn_{0.1}Sb$ and $Mn_{1.96}Zn_{0.04}Sb$ alloys. The choice of the compositions is due to the fact that the single-phase state of the samples cannot be ensured at high Zn contents.

EXPERIMENTAL

The $Mn_{1.9}Zn_{0.1}Sb$ and $Mn_{1.96}Zn_{0.04}Sb$ alloys with the tetragonal Cu_2Sb-type structure were prepared by solid-phase reaction method. Fine manganese, zinc, and antimony powders, which were taken in proportions calculated for the $Mn_{1.9}Zn_{0.1}Sb$ and $Mn_{1.96}Zn_{0.04}Sb$ compositions, were placed in quartz ampoules, which were evacuated to a pressure of 10^{-4} atm and subsequently heated in accordance with regimes described in [10, 11]. Experimental and theoretical studied of the prepared samples were performed. The phase composition was studied by X-ray diffraction analysis at room temperature using Cu$K\alpha$ radiation with the wavelength $\lambda = 0.15406$ nm. The crystal lattice parameters were determined. Magnetic measurements were performed in accordance with induction procedure using a vibrating-sample magnetometer (VSM) (Cryogenic Limited). The isothermal magnetic entropy change in the phase transition temperature range was determined by indirect method using field dependences of magnetization and Maxwell' relations.

RESULTS AND DISCUSSION

The X-ray diffraction analysis showed that the $Mn_{1.9}Zn_{0.1}Sb$ alloy is not single-phase and contains a small amount (≈5–8%) of a hexagonal nickel arsenide phase. It was shown previously [12] that the Mn_2Sb

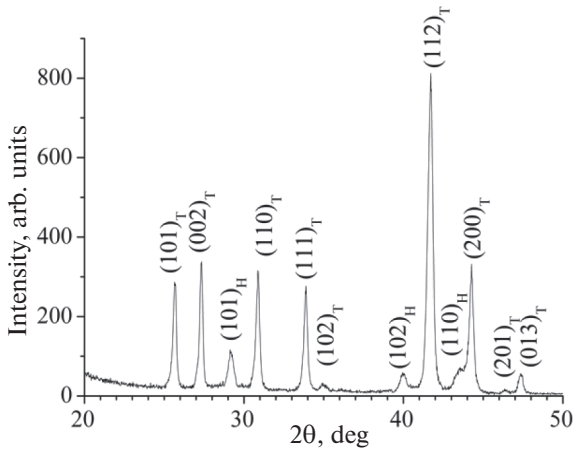

Fig. 1. X-ray diffraction pattern of the $Mn_{1.9}Zn_{0.1}Sb$ alloy.

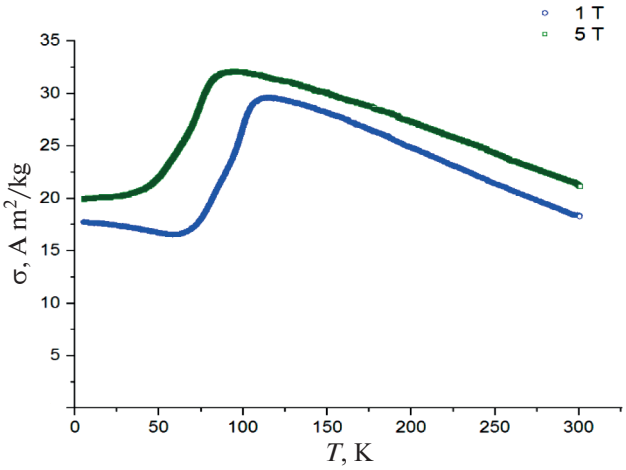

Fig. 2. Temperature dependences of the magnetization of the $Mn_{1.9}Zn_{0.1}Sb$ alloy measured in different magnetic fields.

manganese antimonide always contains nuclei of nickel arsenide phase having the MnSb equiatomic composition; this was found to be typical for the substituted $Mn_{1.9}Zn_{0.1}Sb$ compound. The X-ray diffraction pattern of the prepared alloy (Fig. 1), along with the reflections of the tetragonal phase, contains corresponding weak reflections of the nickel arsenide phase. However, the main phase of the $Mn_{1.9}Zn_{0.1}Sb$ alloy at room temperature is the tetragonal phase with the Cu_2Sb-type structure (space group $P4/nmm$) which lattice parameters are $a = 4.082$ and $c = 6.522$ Å.

Figure 2 shows results of the magnetic measurements of the $Mn_{1.9}Zn_{0.1}Sb$ alloy in a temperature range of ~5–300 K; Fig. 3 shows field dependences of the magnetization measured in fields of 0–10 T.

As is seen from the data given in Figs. 2 and 3, when applying a magnetic field of 1 to 5 T, the sensitivity of characteristic phase transition temperatures is 5.6 K/T; this value is high as compared to those for advanced alloys exhibiting the inverse magnetocaloric effect [13, 14].

During isothermal magnetization, the phase transition from one to another phase is completely induced in a magnetic field of ~6.5 T, which also is the comparable value [14].

ELECTRONIC STRUCTURE OF $Mn_{1.9}Zn_{0.1}Sb$

To study the effect of magnetic order on the electronic structure and interatomic exchange integrals, the Korringa–Kohn–Rostoker relativistic method, coherent potential approximation (KKR-CPA) for a disordered alloy, and SPRKKR v.8.6 software were used [15, 16].

The crystalline potential was calculated in the atomic sphere approximation. To calculate the exchange correlation energy, an approximation that ensures the best coincidence of calculated and experimental magnetic moments was chosen.

In using a local density approximation [17], gradient corrections were not taken into account. Interatomic exchange integrals were calculated by procedure [18] based on calculations of total energy functional variations using a deviation of a selected spin pair from the equilibrium position.

Figure 4 shows the theoretically calculated electronic structure of the $Mn_{1.9}Zn_{0.1}Sb$ alloy in the conception of two structures, namely, ferrimagnetic (FIM) and antiferromagnetic (AF1).

Using X-ray diffraction data, we determine the crystal lattice parameters ($a = 4.082$ and $c = 6.522$ Å); as is seen, the substitution of zinc atoms for a part of manganese atoms leads to the 5% compression of crystal lattice along the c axis (for Mn_2Sb, $a = 4.078$ and $c = 6.557$ Å). In terms of the studied structure type (space group $P4/nmm$), Mn atoms occupy 2a (0, 0, 0)

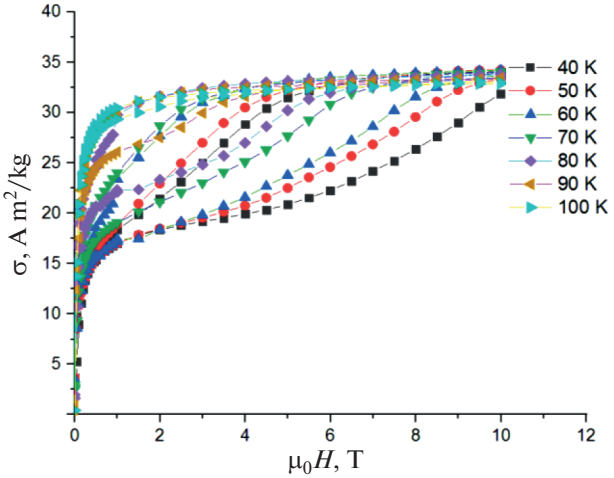

Fig. 3. Field dependences of magnetization of the $Mn_{1.9}Zn_{0.1}Sb$ at a magnetic field change of 0 to 10 T.

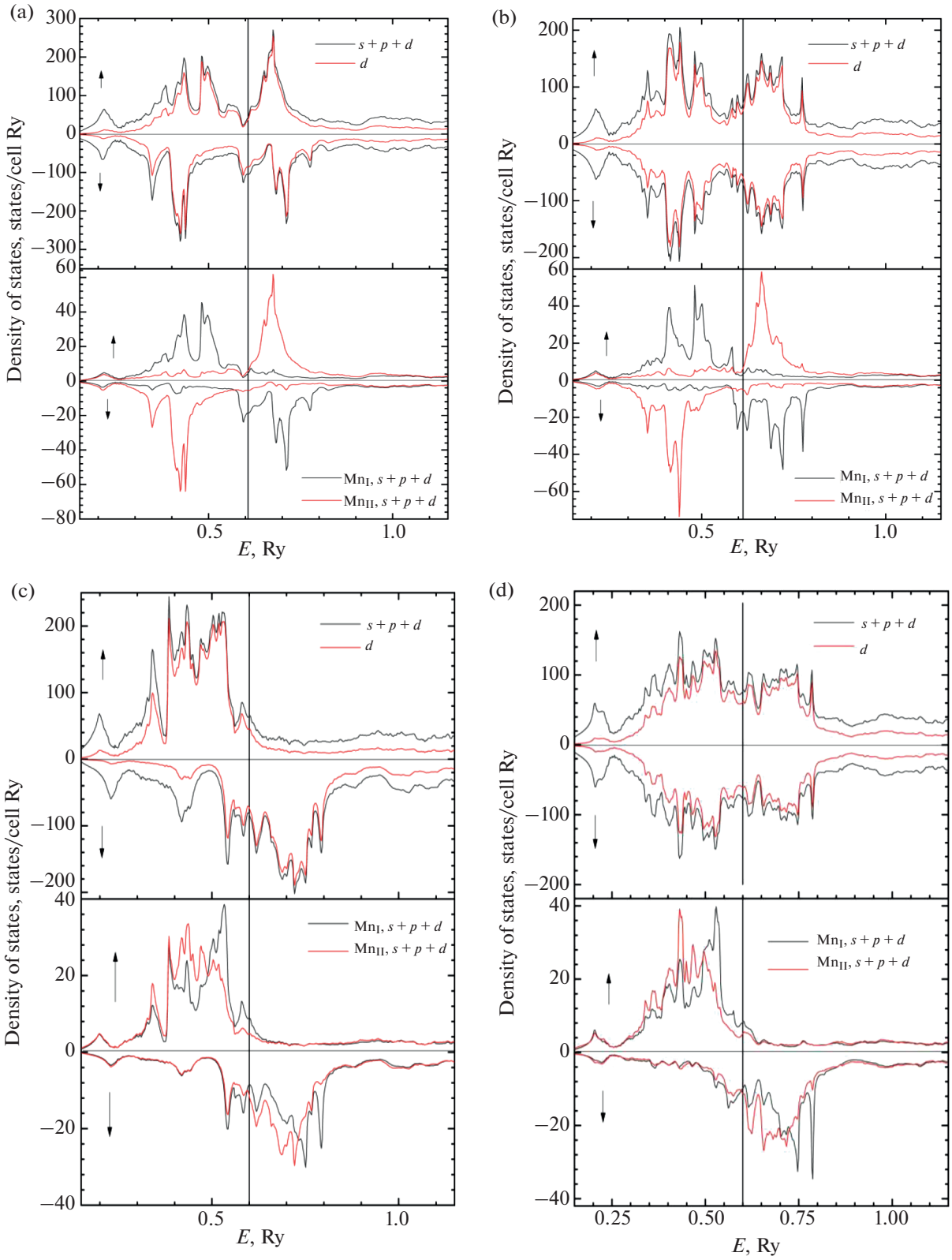

Fig. 4. Density of electron states of the $Mn_{1.9}Zn_{0.1}Sb$ alloy for the (a) ferrimagnetic, (b) AF1 antiferromagnetic, (c) ferromagnetic, and (d) AF2 antiferromagnetic structures; vertical line indicates the Fermi level.

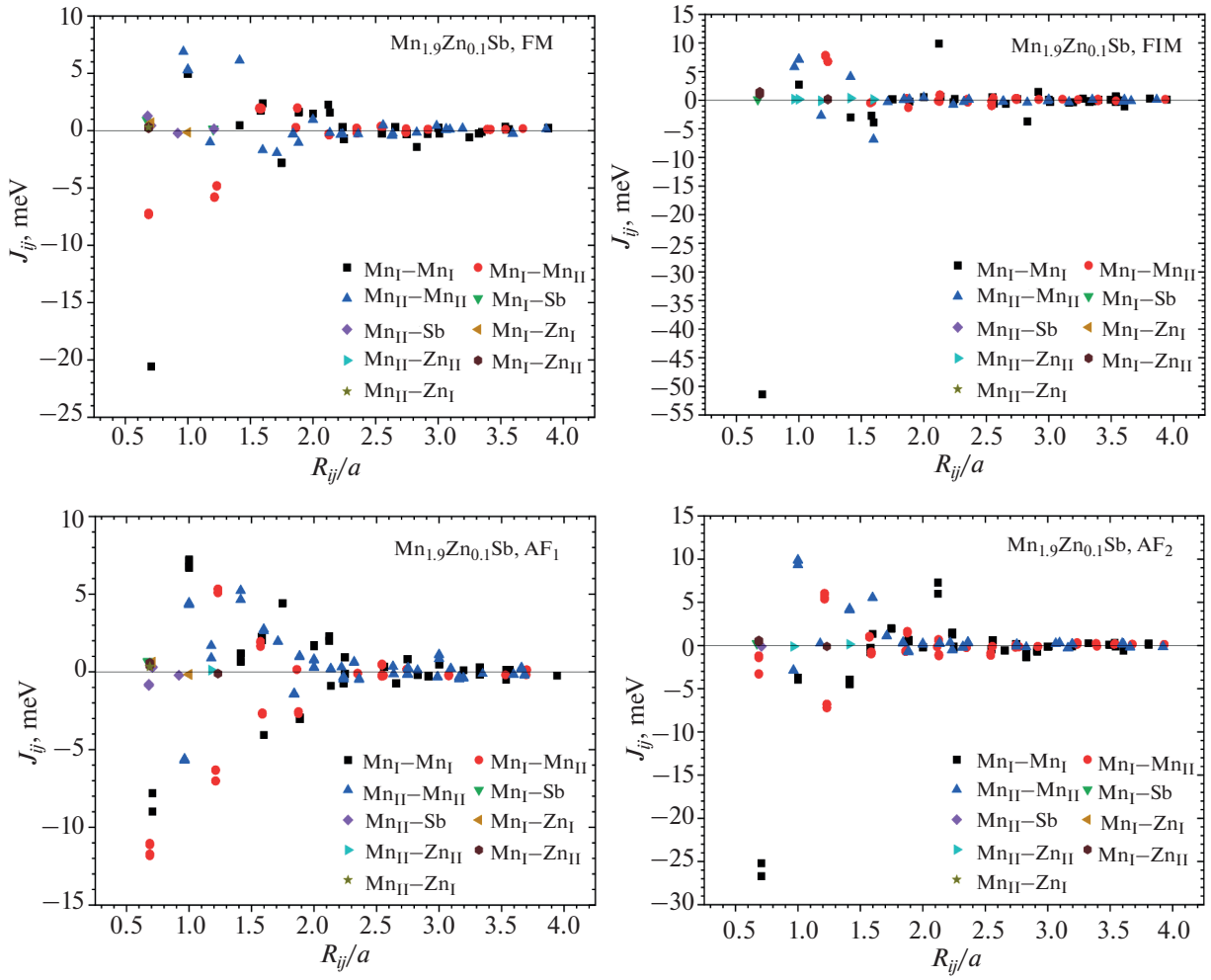

Fig. 5. Dependences of interatomic exchange integrals of the $Mn_{1.9}Zn_{0.1}Sb$ alloy on the interatomic spacing.

and 2*c* (1/4, 1/4, z_1) positions, whereas Sb atoms occupy 2*c* (1/4, 1/4, z_2) positions. Parameters of the positions $z_1 = 0.295$, $z_2 = 0.72$ correspond to the ideal Mn_2Sb structure. Substitutional Zn atoms are assumed to be uniformly distributed at Mn positions.

In performing calculations, four magnetic ordered structures were taken into account; these are ferromagnetic (FM), ferrimagnetic (FIM), and two antiferromagnetic (AF1 and AF2) ones. The orientation of magnetic moments of Mn atoms in the AF1 structure is assumed to be analogous to that in the antiferromagnetic structure in Mn_2As, i.e., the magnetic moments of atoms Mn_I and Mn_{II} located in neighboring layers are arranged antiparallel. The AF2 structure is assumed to be analogous to the antiferromagnetic structure of Fe_2As, i.e., the magnetic moments of Mn_I and Mn_{II} atoms located in neighboring layers are unidirectional [19]. In accordance with the performed calculations, the FIM structure is characterized by the minimum energy (–70840.26092233 Ry), which is followed, in ascending order, by FM (+2.85357 mRy), AF1 (+12.96028 mRy), and AF2 (+54.56484 mRy) structures. The magnetic moments of Mn atoms in corresponding positions are $M(Mn_I) = 3.2\ \mu_B$ and $M(Mn_{II}) = 3.76\ \mu_B$ and can vary in value within 0.1–0.3 μ_B with changing moment orientation. The magnetic moments of zinc and antimony atoms do not exceed 0.1 μ_B.

The typical multipeak structure is observed for the spin-polarized density of electron states, which in whole is characteristic for the 3*d*-metal compounds. It is obvious that *d* electrons of manganese make the main contribution to the formation of the magnetic and transport properties of the alloy. The substantial change in the behavior of the density of electron states of Mn_I near the Fermi level is observed, which is found from the comparison of partial densities of electron states of Mn atoms in the studied magnetic structures. It is possible to assume that the change in the density of states will affect the interatomic Mn_I–Mn_I exchange interactions in the studied alloy. This assumption really is confirmed by direct calculations of interatomic exchange integrals, which were performed for different magnetic structures (Fig. 5).

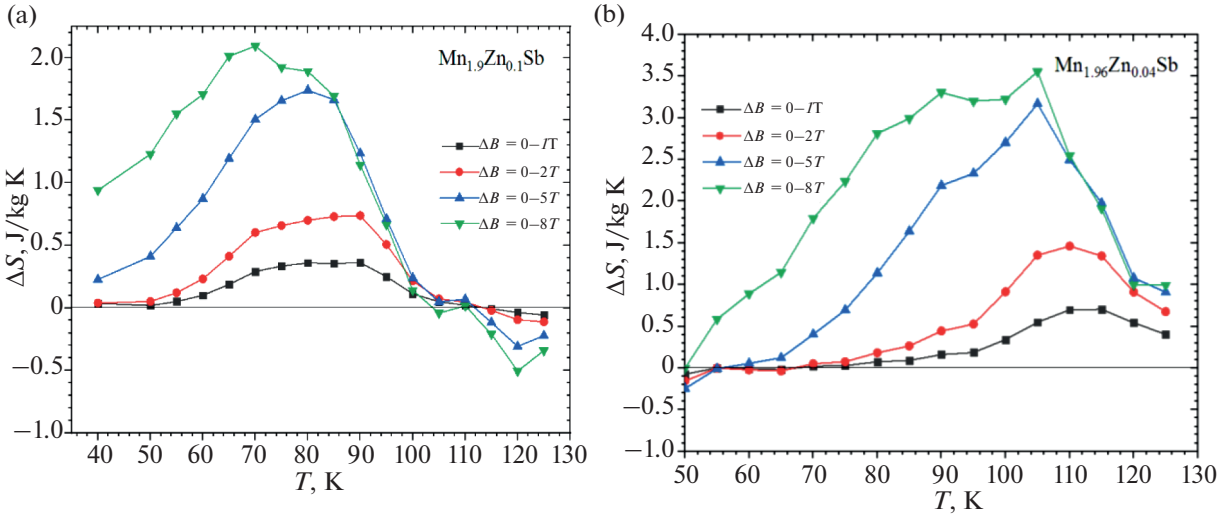

Fig. 6. Temperature dependences of the magnetic entropy change for the (a) $Mn_{1.9}Zn_{0.1}Sb$ and (b) $Mn_{1.94}Zn_{0.06}Sb$ alloys at different magnetic field changes.

In particular, the strong dependence of the exchange interaction of Mn_I–Mn_I atoms located in the basal plane on the magnetic moment of Mn_{II} atom is observed, i.e., J(Mn_I–Mn_I) varies from –20.6 meV for the ferromagnetic structure to –51.4 meV for the ferrimagnetic structure. Moreover, the value of the exchange interaction in the AF1 structure (magnetic moments of neighboring Mn_I and Mn_{II} atoms are parallel) is –9 meV, whereas in the AF2 structure (magnetic moments of neighboring Mn_I and Mn_{II} atoms are antiparallel), it is –26.7 meV. Such a sensitivity of exchange interaction to the magnetic moment orientation of neighboring atom is due to the significant redistribution of electron states of Mn_I and Mn_{II} with changing orientation of their magnetic moments (see Figs. 4a, 4c and 4b, 4d). In short, the "approximation of spin stiffness", which is used in calculating the interatomic exchange interactions [18, 21] in the case of the $Mn_{2-x}Zn_xSb$ system, gives correct results only for slight deviations of local magnetic moments from the initial magnetic structure, which should be taken into account in both theory building and performing simulations.

MAGNETOCALORIC EFFECT

Magnetocaloric characteristics of the studied samples were determined using a series of magnetization curves measured at different temperatures and the Maxwell's relation:

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

Figure 6 shows the obtained temperature dependence of the magnetic entropy change for the $Mn_{1.9}Zn_{0.1}Sb$ and $Mn_{1.96}Zn_{0.04}Sb$ alloys.

The maximum magnetic entropy change for the $Mn_{1.9}Zn_{0.1}Sb$ and $Mn_{1.96}Zn_{0.04}Sb$ compositions is observed at ~70 and ~100–110 K, respectively. At a magnetic field change of 0 to 8 T, the maximum magnetic entropy change for the $Mn_{1.9}Zn_{0.1}Sb$ smple is ~2 J/(kg K).

For the $Mn_{1.94}Zn_{0.06}Sb$ composition, at a magnetic field change of 0 to 8 T, the maximum magnetic entropy change near 100 K is ~3.5 J/(kg K).

The values of the inverse magnetocaloric effect reached for the $Mn_{2-x}Zn_xSb$ system are comparable with those observed for the related alloys, such as $Mn_2Sb_{0.95}Bi_{0.05}$ (2.5 J/(kg K) at 120 K in a field change of 5 T [1]), $Mn_2Sb_{0.95}Ge_{0.05}$ (6 J/(kg K) at 150 K in a field change of 7 T [20]), and $Mn_{1.95}Ge_{0.05}Sb$ (7 J/(kg K) at 180 K in a field change of 7 T [20]). Thus, the alloying with zinc widens the working range of Mn_2Sb-based magnetocaloric materials at cryogenic temperatures in designing cascade magnetic refrigeration systems.

CONCLUSIONS

The experimental studies and theoretical calculations showed that the maximum magnetic entropy change for the $Mn_{1.9}Zn_{0.1}Sb$ alloy in a magnetic field change of 0 to 8 T is ~2 J/(kg K) and corresponds to a temperature of ~70 K. The existence of the magnetic phase transition from the ferrimagnetic to antiferro-

magnetic state leads to the appearance of inverse magnetocaloric effect.

For the $Mn_{1.94}Zn_{0.06}Sb$ alloy, in a magnetic field change of 0 to 8 T, the maximum magnetic entropy change at ~100 K is ~3.5 J/(kg K).

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CONFLICT OF INTEREST

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

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