

Preparation and Characterization of $(\text{MnZn})_{1-x}\text{Fe}_x\text{Sb}$ Solid Solutions with the Cu_2Sb Structure

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Received January 29, 2013; in final form, April 11, 2013

Abstract— $(\text{MnZn})_{1-x}\text{Fe}_x\text{Sb}$ solid solutions with the Cu_2Sb structure have been prepared through heterophase reactions. Their stability range is $0 < x \leq 0.2$. The magnetic interaction in the solid solutions has a ferromagnetic character. The Curie temperature and mass magnetization of the solid solutions have been determined, and the iron dopant has been shown not to participate in magnetic interaction.

DOI: 10.1134/S0020168513120030

INTRODUCTION

Mn_2Sb -based substitutional solid solutions with the Cu_2Sb structure have attracted considerable interest owing to the possibility of producing new materials with various magnetic properties through changes in the crystal structure and electronic subsystem of the parent compound. Mn_2Sb is a ferrimagnet with a Curie temperature of 550 K. The magnetic moments of the manganese atoms on structurally inequivalent sites in this compound, MnI and MnII, differ in magnitude and are opposite in direction (Fig. 1) [1]. Mn_2Sb -based solid solutions containing Zn, Co, Cu, and Cr [2–7] possess a colossal magnetoresistance. Solid solutions of zinc in Mn_2Sb are ferromagnets with a magnetic transition near room temperature and a rather steep temperature dependence of their magnetization. This combination of properties makes these solid solutions potentially attractive for use in magnetic refrigeration systems operating near room temperature. In particular, the transition temperature of MnZnSb is 315 K [8], and this material exhibits an appreciable magnetocaloric effect [9].

Data on the existence of solid solutions with the Cu_2Sb structure in the quaternary system Mn–Zn–Fe–Sb are not available in the literature. At the same time, given the aforementioned practical applications, such solid solutions would be of interest from the viewpoint of the possibility of varying the magnetic parameters of materials in the known ternary solid-solution systems $\text{Mn}_{2-x}\text{Zn}_x\text{Sb}$ and $\text{Mn}_{2-x}\text{Fe}_x\text{Sb}$ [10–13].

The objectives of this work were to prepare $(\text{MnZn})_{1-x}\text{Fe}_x\text{Sb}$ solid solutions with the Cu_2Sb structure and investigate their structural and magnetic properties.

EXPERIMENTAL

To obtain a continuous series of $(\text{MnZn})_{1-x}\text{Fe}_x\text{Sb}$ solid solutions with the Cu_2Sb structure, starting-mixture compositions were calculated under the assumption that iron substitutes for manganese (that is, starting-mixture compositions were calculated for

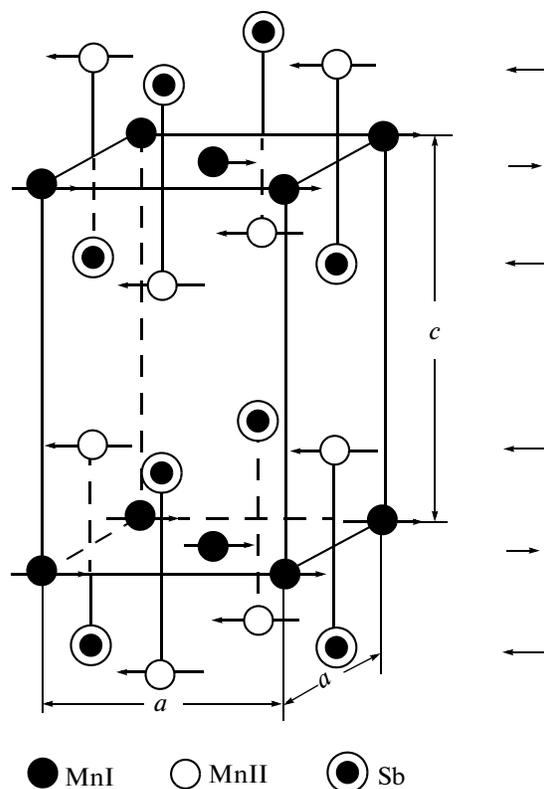


Fig. 1. Magnetic and crystal structures of Mn_2Sb .

Table 1. Lattice parameters and magnetic characteristics of $(\text{MnZn})_{1-x}\text{Fe}_x\text{Sb}$ solid solutions

Material	a , Å	c , Å	$T_C \pm 0.5$, K	$\sigma \pm 0.05$, emu/g
$\text{Mn}_{0.9}\text{ZnFe}_{0.1}\text{Sb}$	4.151	6.192	317	14.55
$\text{MnZn}_{0.9}\text{Fe}_{0.1}\text{Sb}$	4.161	6.206	315	13.77
$\text{Mn}_{0.8}\text{ZnFe}_{0.2}\text{Sb}$	4.149	6.176	305	14.85
$\text{MnZn}_{0.8}\text{Fe}_{0.2}\text{Sb}$	4.135	6.193	310	11.12

the $\text{Mn}_{1-x}\text{Fe}_x\text{ZnSb}$ system) in the composition range $0 \leq x \leq 1$ with a step $\Delta x = 0.1$ and under the assumption that iron substitutes for zinc to give $\text{MnZn}_{1-x}\text{Fe}_x\text{Sb}$ materials. In our preparations, we used spectroscopically pure elemental powders.

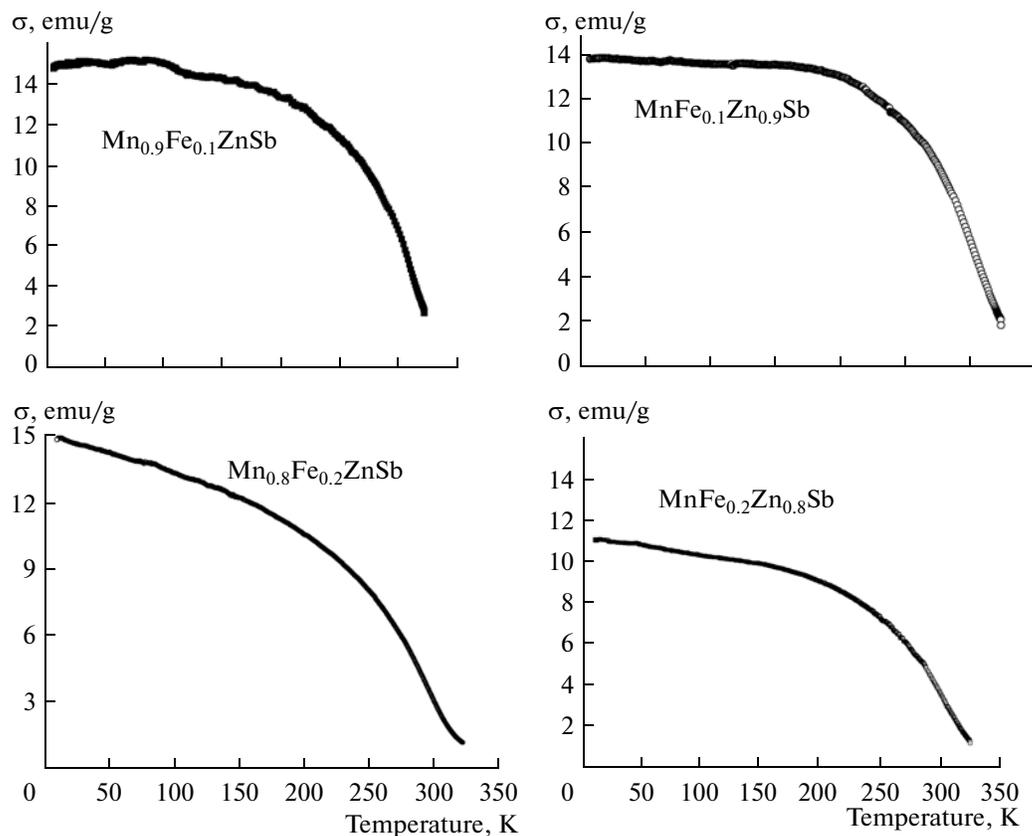
Samples were prepared by heterophase synthesis from an appropriate homogeneous mixture of manganese, iron, zinc, and antimony powders in a single-zone resistance furnace. The mixture was sealed in silica ampules under a vacuum of 0.1 Pa. Since antimony and zinc are low-melting-point metals, the mixture was slowly heated (over a period of 20 h) to 1000°C, the formation temperature of the tetragonal phase in the Mn–

Fe–Zn system. Next, the mixture was held at this temperature for 4 h and then quenched in water.

The phase composition of the synthesis products was determined by X-ray diffraction on a DRON-3M powder diffractometer (CuK_α radiation, scan step of 0.03°, angular range 20°–90°, counting time of 3 s per data point).

Magnetic measurements were performed by an induction technique using a Cryogenic Ltd. vibrating sample magnetometer (VSM). The temperature-dependent mass magnetization of the solid solutions was measured at temperatures from 5 to 320 K in a magnetic field of 1 T. The samples ranged in weight from 0.1 to 0.3 g. Magnetization isotherms of polycrystalline samples were obtained in magnetic fields of up to 14 T.

Mössbauer measurements were performed in a transmission geometry in constant acceleration mode. The gamma source used was $^{57}\text{mCo}(\text{Rh})$. The rated linewidth of the source was 0.11 mm/s. The measurements were made at sample temperatures of 77 and 300 K. The Recoil program was used to more accurately determine parameters of the measured Mössbauer spectra.

**Fig. 2.** Mass magnetization as a function of temperature for $\text{Mn}_{1-x}\text{Fe}_x\text{ZnSb}$ and $\text{MnFe}_x\text{Zn}_{1-x}\text{Sb}$ solid solutions in a magnetic field of 1 T.

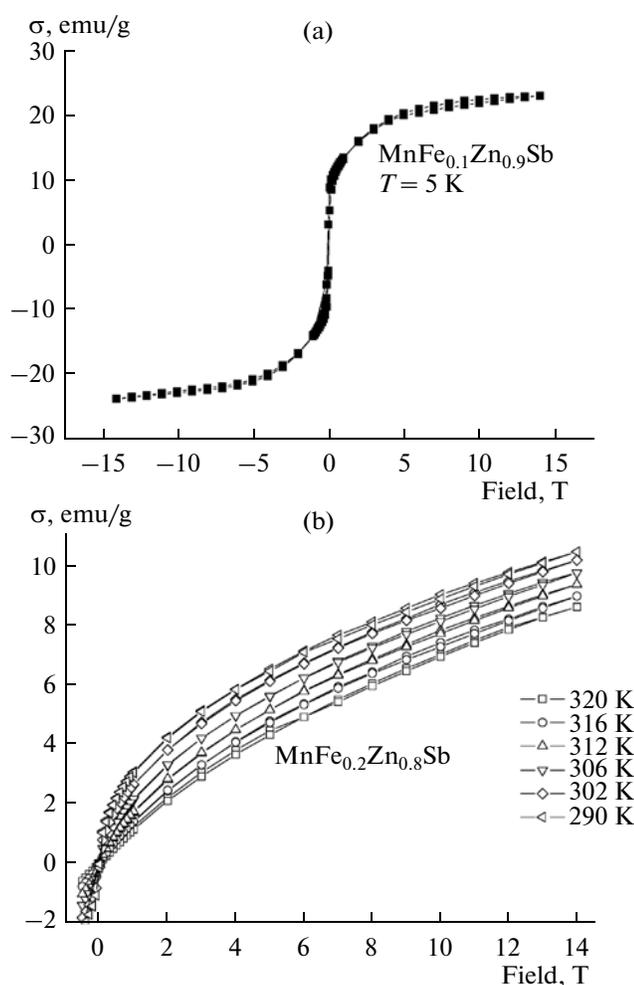


Fig. 3. Field dependences of mass magnetization for $\text{MnFe}_x\text{Zn}_{1-x}\text{Sb}$ solid solutions in magnetic fields of up to 14 T.

RESULTS AND DISCUSSION

The lattice parameters, Curie temperature, and mass magnetization of the solid solutions are presented in Table 1. Their unit-cell parameters were refined using FullProf software. The magnetic phase transition temperatures of the solid solutions were evaluated by extrapolating the linear portion of the plot of the square of their mass magnetization versus temperature to the temperature axis.

X-ray diffraction characterization of the synthesis products indicated limited solubility in the system: at iron contents $x > 0.2$, the X-ray diffraction patterns of the samples showed additional peaks, inconsistent with the Cu_2Sb structure. Thus, we are led to conclude that $\text{Mn}_{1-x}\text{Fe}_x\text{ZnSb}$ and $\text{MnZn}_{1-x}\text{Fe}_x\text{Sb}$ solid solutions with the Cu_2Sb structure exist in the composition range $0 < x \leq 0.2$. The stability limits and lattice parameters of the solid solutions were essentially independent (to within the present measurement uncertainty) of which substitution was assumed in calculating the starting-mixture compositions (Table 1).

The temperature-dependent magnetization measurement results (Figs. 2, 3) demonstrate that the solid solutions possess a magnetic moment up to temperatures slightly higher than room temperature, which differs little from the magnetic phase transition temperature of MnZnSb . The mass magnetization of the solid solutions is on the order of 14 emu/g. According to the magnetic-field dependence of their magnetization (Fig. 3a), the materials can be thought of as soft-magnetic. According to the type of magnetic interaction, the solid solutions are ferromagnets (Figs. 2, 3b).

Figure 4 shows the measured Mössbauer spectra of our samples. The ^{57}Fe Mössbauer spectra of the $\text{Mn}_{0.8}\text{Fe}_{0.2}\text{ZnSb}$ and $\text{MnFe}_{0.2}\text{Zn}_{0.8}\text{Sb}$ solid solutions at $T_{\text{room}} = 300\text{ K}$ and $T_{\text{LN}} = 77\text{ K}$ have no magnetic component. The lack of magnetic splitting means that there is no magnetic field at the ^{57}Fe nuclei. At the same time, macromagnetic measurements indicate that the solid solutions possess magnetization up to room temperature or even slightly above. Since Mössbauer spectroscopy is extremely sensitive to the local environment of a resonance atom, such a situation can occur when the local environment of resonance iron atoms (their nearest and second neighbor environments) is formed by (nonmagnetic) zinc atoms. It may be that the iron resides predominantly on the MII site, which is occupied by the Zn atoms in MnZnSb . The participation of the iron atoms in magnetic interactions would then be blocked, with zero magnetic field at the iron nuclei and a nonmagnetic character of the ^{57}Fe Mössbauer spectrum.

Table 2 lists the Mössbauer effect parameters refined in a single-doublet model. The isomer shift (IS) approaches that reported by Blaauw et al. [14] for the manganese antimonide Mn_2Sb . The quadrupole

Table 2. Mössbauer effect parameters

Material	IS, mm/s	QS, mm/s	W , mm/s	IS, mm/s	QS, mm/s	W , mm/s
	300 K			77 K		
$\text{Mn}_{0.8}\text{Fe}_{0.2}\text{ZnSb}$	0.41 ± 0.03	0.26 ± 0.02	0.14 ± 0.01	0.57 ± 0.06	0.27 ± 0.04	0.16 ± 0.04
$\text{MnFe}_{0.2}\text{Zn}_{0.8}\text{Sb}$	0.40 ± 0.04	0.25 ± 0.05	0.16 ± 0.05	0.60 ± 0.07	0.43 ± 0.05	0.18 ± 0.04

Note: IS is the isomer shift of the subspectrum relative to metallic iron, QS is the quadrupole splitting of the lines of the doublet, and W is the linewidth.

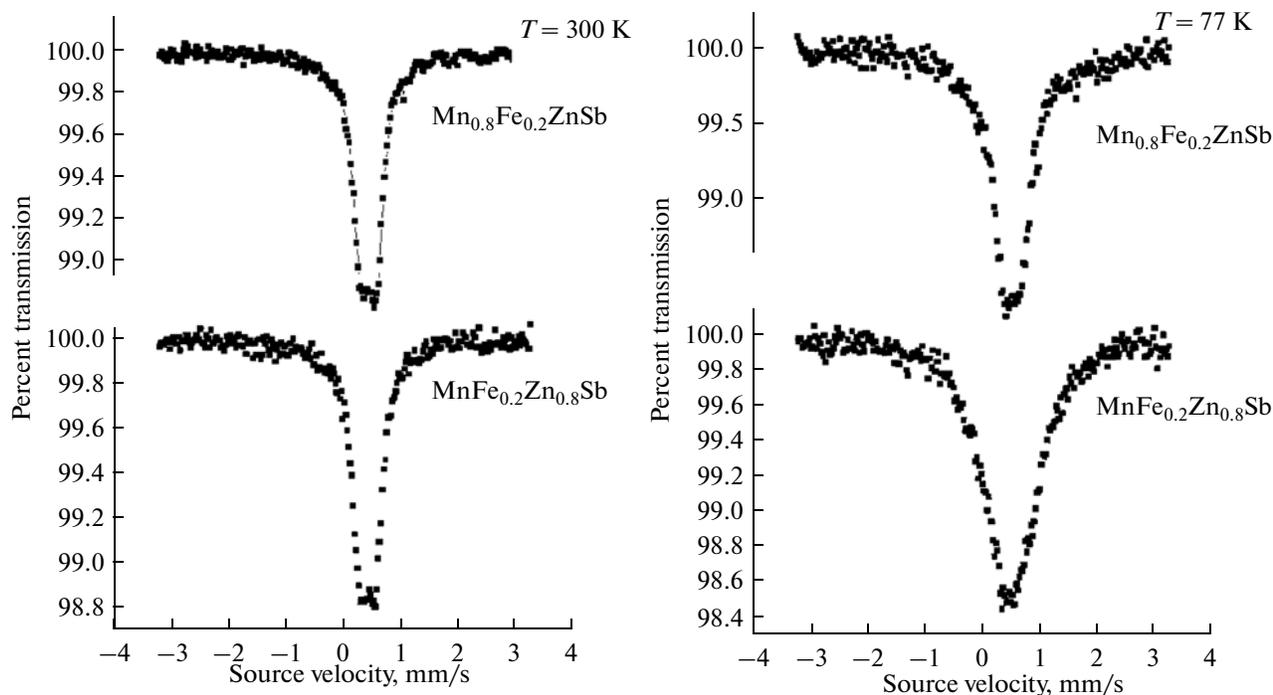


Fig. 4. Measured Mössbauer spectra of the $\text{Mn}_{0.8}\text{Fe}_{0.2}\text{ZnSb}$ and $\text{MnFe}_{0.2}\text{Zn}_{0.8}\text{Sb}$ solid solutions at $T = 300$ and 77 K.

splitting (QS) in the spectra agrees with the QS of resonance iron atoms in octahedral coordination [15, 16]. Both the IS and QS vary little with composition. The slightly larger shift of the line at 77 K in comparison with 300 K is due to the contribution of the temperature-dependent second-order Doppler shift. The linewidth in the 77 -K spectrum is greater than the rated linewidth of the gamma source ($W_{\text{st}} \approx 0.11$ mm/s). The broadening of the lines may be caused by an inhomogeneous local environment of the ^{57}Fe resonance atoms. At 77 K, another possible reason for the broadening is that the doublet is overlapped by internal lines of a hardly discernible magnetic subspectrum with an extremely low intensity.

On the whole, a rather intriguing result of the present Mössbauer measurements is the lack of magnetic interactions at the iron atoms, suggesting that a more detailed study is needed.

CONCLUSIONS

$(\text{MnZn})_{1-x}\text{Fe}_x\text{Sb}$ solid solutions with the Cu_2Sb structure have been prepared through heterophase reactions. The stability range of the solid-solution phase is $0 \leq x \leq 0.2$.

According to magnetization measurements as a function of magnetic field and temperature, magnetic interactions in the $(\text{MnZn})_{1-x}\text{Fe}_x\text{Sb}$, $0 < x \leq 0.2$ solid-solution system have a ferromagnetic character. The

data were used to evaluate the Curie temperature and mass magnetization of the solid solutions.

^{57}Fe Mössbauer spectroscopy results indicate that there are no magnetic interactions at the iron atoms in the $(\text{MnZn})_{1-x}\text{Fe}_x\text{Sb}$ solid solutions.

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Translated by O. Tsarev