

Effect of thermobaric treatment on magnetic characteristics of MnZnSb and $\text{MnZn}_{1-x}\text{Cr}_x\text{Sb}$ ($0 \leq x \leq 0.20$) solid solutions

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Abstract

The paper studies the effect of high-temperature treatment on structural and magnetic properties of the system $\text{MnZn}_{1-x}\text{Cr}_x\text{Sb}$ ($0 \leq x \leq 0.20$) solid solutions obtained by solid-phase reactions with subsequent quenching. It was shown all solid solutions have a tetragonal crystal structure with $P4/nmm$ space group, which is preserved under high-temperature treatment. The temperatures of the magnetic phase transition increase with grow substitution concentration. High-temperature treatment of the initial MnZnSb compound leads to increasing of Curie temperature and coercive force. The effect of substitution concentration on the coercive force and magnetization value has been discovered.

Keywords

solid solutions; antimonides; crystal structure; magnetization; thermobaric treatment

1. Introduction

Magnetoelectric coupling leads to electric polarization change when an external magnetic field is applied and, versa, changing of magnetization with external electric field applied. The effect provides a possibility to create memory elements and devices based on quantum effects. However, candidates for magnetic phase change materials, such as diluted magnetic semiconductors, demonstrate weak ferromagnetism. Control of magnetization by an electric field is possible for metals, but only for an extremely small magnetic (volume and therefore)

signal [1]. One of the interesting compounds in terms of complete and reversible ferromagnetism switching is the bulk intermetallic compound MnZnSb [2, 3]. Relatively high specific magnetization, Curie temperature near room temperature, strong spin polarization and high thermo-EMF values make MnZnSb and based on its solid solutions promising candidates for practical use in a wide range of applications, such as spintronics, magnetocalorics (spin valves, spin transistors, energy-efficient cooling systems for various applications, including household refrigerators, air conditioners, cryogenic systems, etc.) [3, 4].

MnZnSb compound has a tetragonal crystal structure of the Cu_2Sb type. In such structure Mn atoms are located in planes perpendicular to the c axis, and between the nearest manganese planes there are layers of non-magnetic Zn and Sb [3–5]. Obviously, there is a strong direct exchange bond of manganese atoms in perpendicular planes and a relatively weak bond through two planes of non-magnetic atoms, so MnZnSb has interesting magnetic properties. The Curie temperature (T_C) for MnZnSb is 312 K, and the magnetic moment of the manganese atom is 1.5 μB , which is significantly less than the calculated value for a localized Mn atom [1, 6]. Exposing of high pressures can initiate phase transitions of the MnZnSb crystal structure, which leads to a change of magnetic characteristics or a band structure of the compound.

There is very few information in the literature about the existence of solid solutions with a Cu_2Sb -type structure in quaternary systems based on MnZnSb. At the same time, these solid solutions are interesting for given above prospects for practical application, due to the possibility of magnetic parameters varying by substitution. For example, the authors of [7, 8] showed that $\text{MnZn}_{1-x}\text{Fe}_x\text{Sb}$ compounds are ferromagnetic and have a solubility limit of $x = 0.2$. The results of Mössbauer spectroscopy on ^{57}Fe nuclei at $T = 77$ and 300 K indicate an absence of magnetic interactions of iron atoms in $\text{MnZn}_{1-x}\text{Fe}_x\text{Sb}$ solid solutions. Thus, it has been shown a number of new materials with improved characteristics can be obtained by replacing zinc atoms with iron atoms giving opportunity to create materials for specific practical applications.

Obtaining experimental data is important for constructing models of the formation of unique properties of new types of magnetic materials, and can be used for theoretical ab-initio calculations. In addition, this will allow developing new concepts and models of structural ordering, which makes it possible to synthesize new functional materials with specified physical properties. The aim of this work was to synthesize solid solutions of the $\text{MnZn}_{1-x}\text{Cr}_x\text{Sb}$ system ($0 \leq x \leq 0.20$) by replacing zinc atoms with chromium atoms, including under high pressure and temperatures, to study their crystal structure and the possibility of controlling magnetic characteristics with a magnetic field and concentration.

2. Materials and experimental methods

The initial MnZnSb compound and $\text{MnZn}_{1-x}\text{Cr}_x\text{Sb}$ ($0 \leq x \leq 0.20$) solid solutions were synthesized using solid-phase reactions. The initial chemical elements used to obtain the samples had the following purity characteristics: manganese – 99.96%, zinc, chromium and antimony – 99.99%. The calculated amounts of the initial components were thoroughly mixed, poured into ampoules, which were then evacuated to a residual pressure of $\sim 10^{-2}$ Pa and sealed. The samples were heated up to 1020 K with a

heating rate ~ 100 K/h and kept at the temperature for 20–24 h. Then, the samples were quenched in water. The ingots removed from the ampoules were silvery with metallic luster, very brittleness and their surface contained numerous small cavities and pores. The obtained samples were subjected to thermobaric treatment under pressure ~ 5.0 GPa, and the temperature ~ 623 K for 120 s.

The crystal structure and phase composition of the samples were certified at room temperature using X-ray diffraction method in CuK_α radiation. The structural parameters were calculated using the FullProf program. The temperature dependences of the specific magnetization were obtained using the ponderomotive method in a magnetic field with an induction of 0.86 T. The field dependences of the specific magnetization were studied using a Cryogenic Ltd. vibration magnetometer (VSM) in a magnetic field of up to ± 10 T and at a temperature of 5 K.

3. Results and discussion

Analysis of X-ray diffraction data showed that the MnZnSb compound and $\text{MnZn}_{1-x}\text{Cr}_x\text{Sb}$ ($0 \leq x \leq 0.20$) solid solutions have a tetragonal crystal structure of the Cu_2Sb (anti-PbFCl) type, with a $P4/nmm$ space group. The unit cell of MnZnSb (Fig. 1) contains three formula units: Mn atoms occupy the Wyckoff position $2a$, Zn atoms occupy the position $2c$, and Sb atoms occupy the position $4f$. Each Mn atom is surrounded by six Zn atoms and conversely. Sb atoms form a distorted face-centered lattice connecting the Mn and Zn sublattices.

Phase analyses demonstrated an existing of single-phase $\text{MnZn}_{1-x}\text{Cr}_x\text{Sb}$ solid solutions in $x \leq 0.20$ concentration range. No new Bragg peaks were observed on X-ray patterns after treatment under high pressure (Fig. 2), however Bragg peaks become wider and ratio intensities of peaks was changed. It can be assumed that the after treatment structure became less ordered. The parameters of unit cell and c/a ratio of studying solid solutions

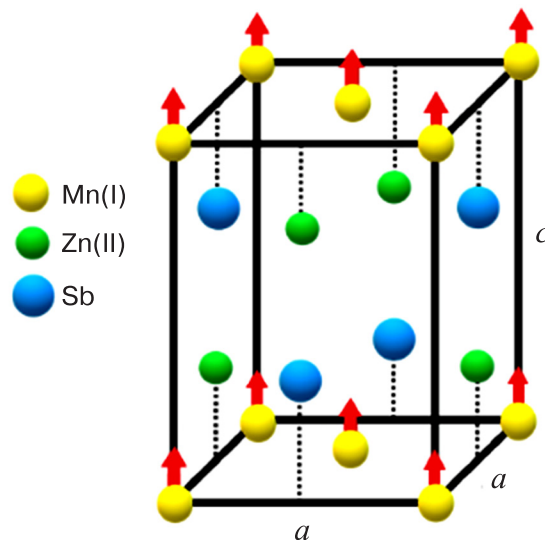


Figure 1. Crystal structure of MnZnSb

Table 1. Calculated values of a and c lattice parameters, the c/a ratio and elementary cell volumes of the system $\text{MnZn}_{1-x}\text{Cr}_x\text{Sb}$ solid solutions

x	Before thermobaric treatment			After thermobaric treatment		
	a (nm)	c (nm)	c/a	a (nm)	c (nm)	c/a
0.00	0.417	0.625	1.497	0.418	0.627	1.496
0.05	0.417	0.626	1.502	0.417	0.626	1.501
0.10	0.416	0.626	1.504	0.416	0.626	1.505
0.20	0.416	0.627	1.507	0.415	0.625	1.511

before and after high pressure treatments are given in Table 1. With an increase in the substitution concentration, a smooth decrease in the value of the parameters a and c was observed.

Figure 3 shows temperature dependences of magnetization of the $\text{MnZn}_{1-x}\text{Cr}_x\text{Sb}$ ($0 \leq x \leq 0.20$) solid solutions before and after high-pressure treatment. A specific magnetization becomes close to zero at 350 K for initial MnZnSb compound, however an anomaly of specific magnetization behavior is observed in the temperature range of 400–600 K. This can be explained by realization of a two-phase magnetic state corresponding to two crystalline homogeneous regions with different magnetic ordering patterns [9]. In this work, using a neutron diffraction method for the initial MnZnSb compound, the authors observed of local inhomogeneities in atoms and structural vacancy, which contributes to appearance of individual magnetically ordered clusters. The long-range magnetic order determined by the main three-dimensional magnetic structure is broken at the temperature around 320 K. However, some separated clusters remain in the

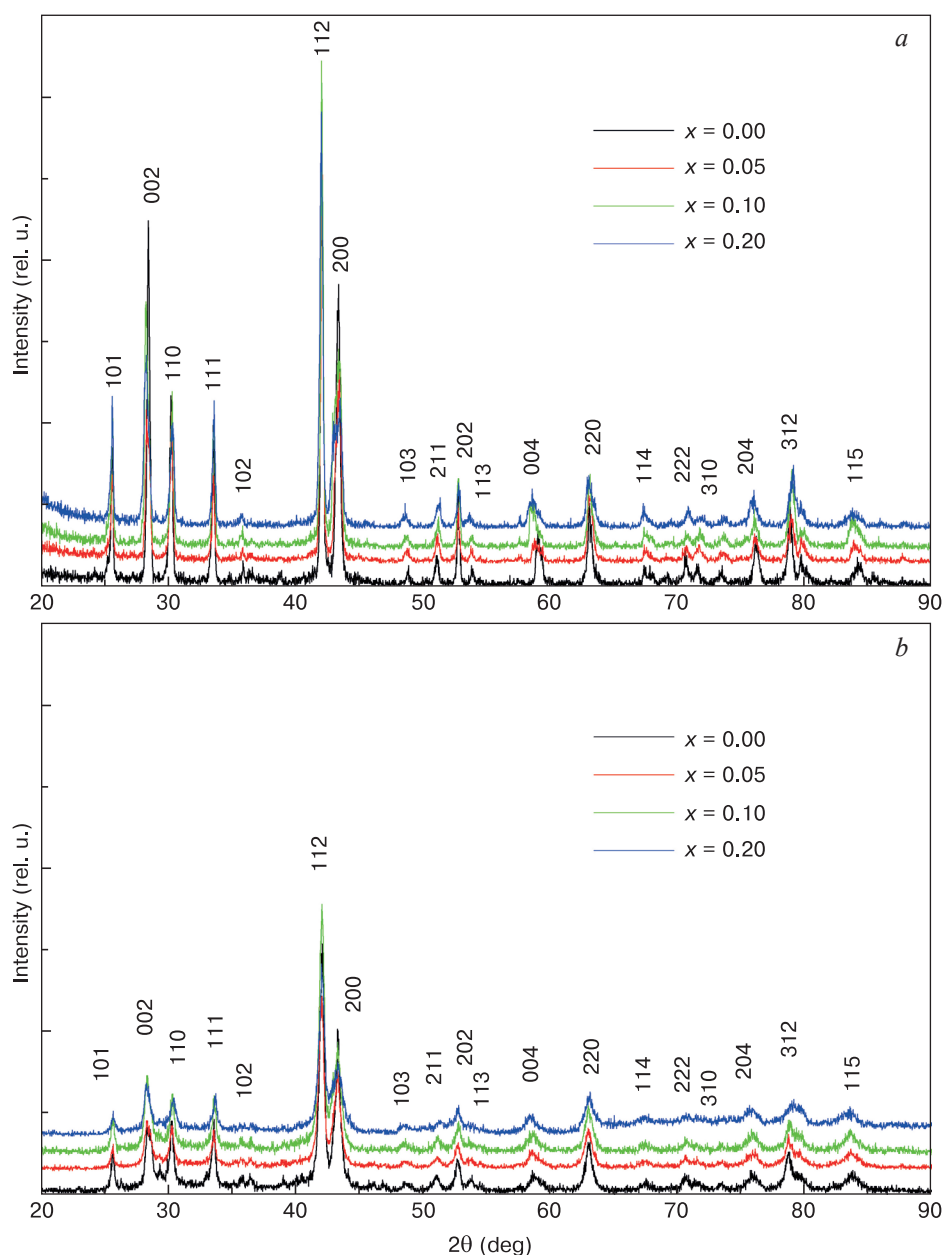


Figure 2. X-ray diffraction patterns of the $\text{MnZn}_{1-x}\text{Cr}_x\text{Sb}$ system solid solutions before (a) and after thermobaric treatment (b)

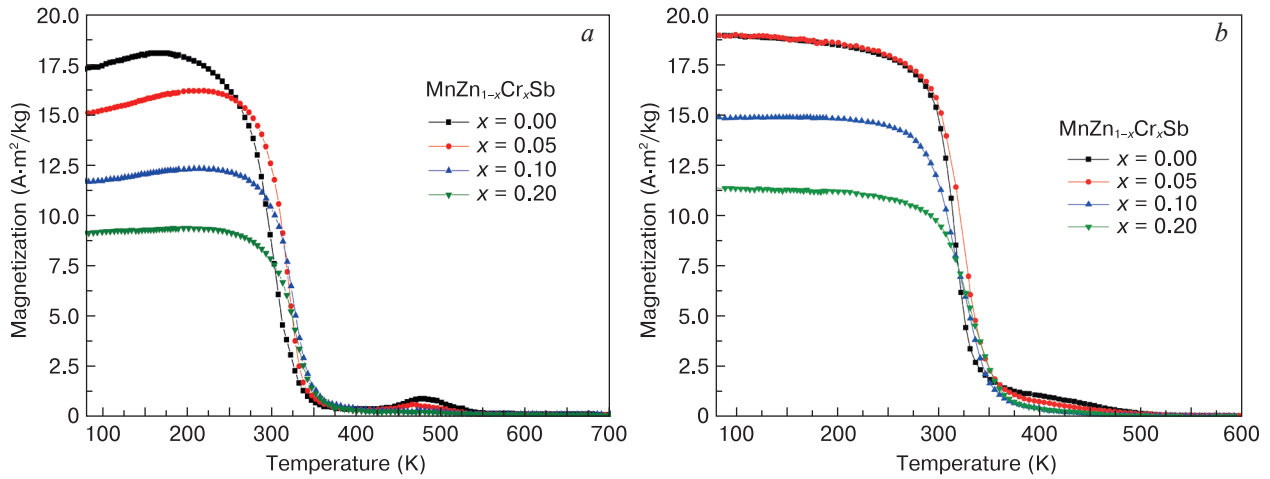


Figure 3. Temperature dependences of the specific magnetization of $\text{MnZn}_{1-x}\text{Cr}_x\text{Sb}$ solid solutions before (a) and after (b) thermobaric treatment

matrix of other manganese ions. They give a small resulting moment at $T > 320$ K. With a further temperature increase, all magnetic clusters undergo to paramagnetic state.

One can see from the figure the anomaly observed in the range of 400–600 K for both pure MnZnSb and its solid solution $\text{MnZn}_{1-x}\text{Cr}_x\text{Sb}$ ($x = 0.05$) disappears as after thermobaric treatment as with an increasing of chromium concentration. This fact might be due to absence

of individual magnetically ordered clusters formation for these compounds. High pressure and temperature treatment leads to the disappearance of structural inhomogeneities and, as results, clusters with a small resulting moment. Increasing of chromium concentration, most likely, has an opposite effect and lead to more structural defects. The Curie temperatures of the solid solutions were determined by extrapolating of linear part of the specific magnetization square values temperature dependence to

Table 2. Values of the average magnetic moments at 80 K ($\mu_{80\text{K}}$), Curie temperature (T_C), saturation magnetization (σ_s), residual magnetization (σ_r) and coercivity (H_C) for $\text{MnZn}_{1-x}\text{Cr}_x\text{Sb}$ solid solutions

x	Before thermobaric treatment					After thermobaric treatment				
	$\mu_{80\text{K}}, \mu_B$	T_C (K)	σ_s, μ_B	σ_r, μ_B	H_C (kOe)	$\mu_{80\text{K}}, \mu_B$	T_C (K)	σ_s, μ_B	σ_r, μ_B	H_C (kOe)
0.00	0.72	313	0.75	0.41	0.45	0.82	323	0.97	0.62	4.1
0.05	0.65	318	0.65	0.24	0.41	0.82	326	0.95	0.60	3.1
0.10	0.51	323	0.51	0.19	0.40	0.64	330	0.79	0.46	2.6
0.20	0.39	333	0.40	0.15	0.39	0.49	337	0.70	0.34	2.6

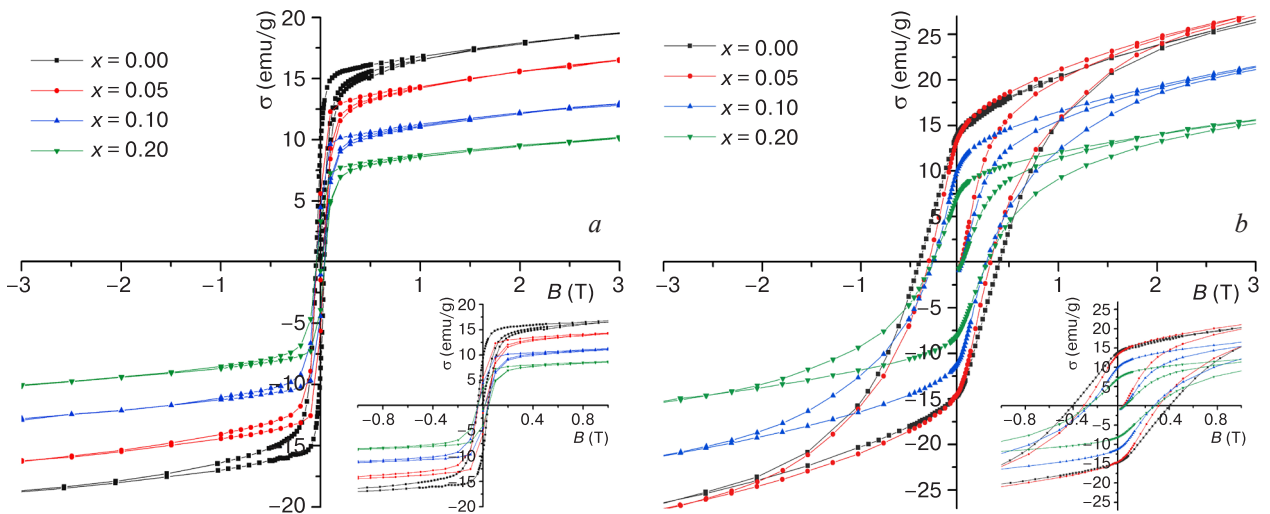


Figure 4. Field dependences of specific magnetization before (a) and after (b) thermobaric treatment for $\text{MnZn}_{1-x}\text{Cr}_x\text{Sb}$ solid solutions at 5 K

the temperature axis $\sigma^2 = f(T)$. It was found the Curie temperatures increases with an increasing of chromium concentration from 313 K for initial MnZnSb to 333 K for MnZn_{0.80}Cr_{0.20}Sb and magnetic moment value decreases from 0.72 μ_B ($x = 0$) to 0.39 μ_B ($x = 0.20$). The values of fundamental magnetic quantities for the initial MnZnSb compound and the obtained solid solutions are given in Table 2.

Figure 4 presents the magnetization field dependences of MnZn_{1-x}Cr_xSb ($0 \leq x \leq 0.20$) solid solutions at 5 K before and after thermobaric treatment. Based on magnetic field dependences it was found the magnetization of all solid solutions saturates in a magnetic field of ~ 2 T. A coercivity (H_C) for all compositions was determined from the hysteresis loops (insert to Fig. 4, Table 2). It was found the coercivity of the initial alloy was 440 Oe. The coercivity of all compositions before high-pressure treatment was about 0.4 kOe. The H_C values decreases for samples before thermobaric treatment, and increases after one with an increase in the substitution concentration. An increasing of specific magnetization value, Curie temperature, and saturation magnetization was also found as a result of thermobaric treatment for studied solid solutions (Table 2). Treatment of the compounds with high pressure leads to a decrease in the average size of the grains as well as to anisotropic changes in their shape thus leading to a modified morphology of the grains. The structural changes occurred in the compounds subjected to high pressure treatments are confirmed by a variation of the XRD diffraction patterns, viz. the reflections intensities are modified, width of the peaks notably increases (see Fig. 2). The mentioned modification in the grains morphology increases magnetic anisotropy and thus leads to an increased coercivity of the compounds (Fig. 4).

Disclosure statement

The authors report there are no competing interests to declare.

References

- Greve M.M., Das B., Issac I., Witter R., Wang D., Kruk R., Hahn H., Dasgupta S. Electric-potential-induced complete control of magnetization in MnZnSb metallic ferromagnets. *Advanced Functional Materials*. 2021; 7(1): 2000790. <https://doi.org/10.1002/aefm.202000790>
- Azouaoui A., Mouchou S., Toulal Y., Rezzouk A., Benzakour N., Hourmatallah A. DFT and Monte Carlo simulations of the intermetallic compound MnZnSb. *Molecular Physics*. 2024; e2427238. <https://doi.org/10.1080/00268976.2024.2427238>
- Dinkar D.K., Palit M., Gopalan R., Das B. Magnetocaloric properties and critical exponents in anti-PbFCI type ZnMnSb room temperature ferromagnet prepared via different routes. *Journal of Magnetism and Magnetic Materials*. 2019; 489: 165437. <https://doi.org/10.1016/j.jmmm.2019.165437>
- Pankratov N.Yu., Mitsiuk V.I., Ryzhkovskii V.M., Nikitin S.A. Direct measurement of the magnetocaloric effect in MnZnSb intermetallic compound. *Journal of Magnetism and Magnetic Materials*. 2019; 470: 46–49. <https://doi.org/10.1016/j.jmmm.2018.06.035>
- Nabi M.R.U., Basnet R., Pandey K., Chhetri S.K., Upreti D., Acharya G., Wang F., Fereidouni A., Churchill H.O.H., Guan Y., Mao Z., Hu J. Coupling between magnetic and transport properties in magnetic layered material Mn_{2-x}Zn_xSb. *Acta Materialia*. 2023; 259: 119251. <https://doi.org/10.1016/j.actamat.2023.119251>
- Murgatroyd P.A.E., Routledge K., Durdy S., Gaultois M.W., Surta T.W., Dyer M.S., Claridge J.B., Savvin S.N., Pelloquin D., He-

4. Conclusions

The MnZnSb compound and system MnZn_{1-x}Cr_xSb ($0 \leq x \leq 0.20$) solid solutions were obtained by solid-phase reactions method with subsequent annealing and thermobaric treatment. It was found that all prepared solid solutions have a tetragonal crystal structure (space group $P4/nmm$). It was found that high-pressure treatment has no effect on microstructure of the synthesized compounds, but increases the magnetic characteristics of the samples. Curie temperature rises with an increase in the chromium concentration and after thermobaric treatment. A second-order phase transition is observed at temperature of 313 K for the initial MnZnSb, the temperature increases with an increasing of substitution concentration up to 333 K for MnZn_{0.80}Cr_{0.20}Sb. The disappearance of the high-temperature anomaly with an increasing of chromium concentration and high-pressure treatment was established. The high-pressure treatment leads to an increasing of specific magnetization value and coercivity to 4 kOe and 2.7 kOe for MnZnSb and MnZn_{0.80}Cr_{0.20}Sb, respectively. Thermobaric treatment can be considered as an effective method for changing the value of the main magnetic characteristics, as well for the temperature range of the phase magnetic transition expanding.

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- bert S., Alaria J. Chemically controllable magnetic transition temperature and magneto-elastic coupling in MnZnSb compounds. *Advanced Functional Materials*. 2021; 31(17): 2100108. <https://doi.org/10.1002/adfm.202100108>
7. Rimskii G.S., Yanushkevich K.I., Belozerova N.M. Crystal structure and magnetic characteristics of solid solutions $\text{Mn}_{1-x}\text{Fe}_x\text{NiGe}$. *Physics of the Solid State*. 2021; 63: 485. <https://doi.org/10.1134/S106378342103015X>
8. Budzyński M.Z., Mitsiuk V.I., Surowiec Z.T., Tkachenka T.M. Preparation and Characterization of $(\text{MnZn})_{1-x}\text{Fe}_x\text{Sb}$ solid solutions with Cu_2Sb structure. *Inorganic Materials*. 2013; 49: 1170. <https://doi.org/10.1134/S0020168513120030>
9. Dymont V.P., Makovetsky G.I., Ryzhkovsky V.M. Phase diagram of the magnetic state of a solid solution system $\text{Mn}_{2-x}\text{Zn}_x\text{Sb}$ ($0 \leq x \leq 1.0$). *Fizika tverdogo tela*. 1994; 36(10): 2916. (In Russ.)