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Structure and magnetic properties of MnSb(Zn) and MnSb(Cu) solid solutions

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Abstract

The MnSb(Zn) and MnSb(Cu) solid solutions with NiAs-type of crystal structure have been obtained. The existence regions of mono-phase solutions have been determined. Zn and Cu can substitute 10% atomic for Mn. On the basis of magnetic measurements it was supposed that the Cu or Zn atoms preferable occupy the MeII sites of NiAs-structure if the amount of nonmagnetic substitution not exceed 10% atomic. The preferable occupation of MeII sites by nonmagnetic atom manifests in rising of the Curie temperature of solid solutions relatively unsubstituted alloy. © 2007 Elsevier B.V. All rights reserved.

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1. Introduction

The manganese antimonide and solid solutions on its basis have the NiAs-type of crystal structure [1]. The ideal NiAs structure represents the frame of hexagonal close packing metalloid atoms where the octahedral sites are occupied by metal atoms (MeI), and the interstitials (called trigonal–bipyramidal, or MeII) considered to be completely free. Manganese antimony is characterized by the wide range of homogeneity nearby an equiatomic state, Mn_{1+x}Sb $0 \leq x \leq 0.22$. Being in excess relative to Sb content, Mn atoms partly occupy the MeII positions and the excess or the deficiency of metal in the compound, relative to Sb content, leads to a variety of physical characteristics and parameters within the one-phase limits [2–4]. For example, manganese antimonide is a ferromagnetic compound, but the spontaneous magnetization and also Curie temperature of Mn_{1+x}Sb decrease linearly with increase of x , the empiric correlation is concluded in [3], $T_C = (577 - 790 \times x)\text{K}$.

The solid solution formation between MnSb and transition metals is possible [5], but there is no data published on Cu or Zn diluting in manganese antimony with NiAs-type of structure.

Some investigation of the Cu-substituted manganese–antimony films is presented in Ref. [6].

The objectives for the study are (i) to perform substitutions in the manganese antimonide, namely, to substitute nonmagnetic Cu and Zn for Mn, (ii) to find the solubility limits for the substitutes and (iii) to investigate the effect of the substitutions on the local structure and magnetic properties of MnSb(Zn) and MnSb(Cu) solid solutions.

2. Experimental

Primarily substituted samples were obtained by the procedure described in [1] for the manganese antimony with NiAs-type of crystal structure. The component hangings for the samples have been taken on the basis of the formula $\text{Mn}_{1.1-x}\text{Me}_x\text{Sb}$, where Me = Cu or Zn, and $0 < x < 0.5$. Each synthesis products were analyzed for the phase composition by powder X-ray analysis and unit cell dimensions were obtained in the same way. The roentgenograms were adjusted by the Rietveld method.

The compositions and the phase structure of the synthesized Cu-containing products are given in Table 1.

Lot of tentative synthesizing of MnSb substituted with Cu or Zn, brought to the optimal treatment regime for mono-phase solid solutions receiving between MnSb and Cu or Zn. It is the follows:

1. Slow (during the 24 h) heating up to alloying temperature $T = 900\text{--}950^\circ\text{C}$ of the homogeneous mixture of the appropriate quantities of spectroscopically pure initial components in silica tubes with inner pressure of 10^{-3} Torr.
2. Alloying at $T = 900\text{--}950^\circ\text{C}$ during 4 h.

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Table 1
Phase composition of synthesis products of $\text{Mn}_{1.1-x}\text{Me}_x\text{Sb}$ substituted by Cu

x	Composition (formula)	Phase type
0	$\text{Mn}_{1.1}\text{Sb}$	<i>P63/mmc</i> (194)-hexagonal (single phase)
0.1	$\text{Mn}_{1.0}\text{Cu}_{0.1}\text{Sb}$	<i>P63/mmc</i> (194)-hexagonal (single phase)
0.2	$\text{Mn}_{0.9}\text{Cu}_{0.2}\text{Sb}$	<i>P63/mmc</i> (194)-hexagonal + <i>Fm3m</i> -cubic (MnSb + Cu) (2 phase, weak sign of second phase)
0.3	$\text{Mn}_{0.8}\text{Cu}_{0.3}\text{Sb}$	<i>P63/mmc</i> (194)-hexagonal + <i>Fm3m</i> -cubic (MnSb + Cu) (2 phase, appreciable increase of second phase)
0.4	$\text{Mn}_{0.7}\text{Cu}_{0.4}\text{Sb}$	Multi-phase

- Slow cooling (during 4–5 h) from 950 °C down to 840–860 °C (the temperature of NiAs-phase formation).
- Annealing at $T = 840\text{--}860$ °C during 24 h.
- Water quenching.

The solubility of Cu and Zn in MnSb with NiAs-type of crystal structure appears to be 10% atomic. The X-ray analysis results are shown at Fig. 1.

The structural characteristics of some solid solutions obtained listed in Table 2.

Specific magnetization and saturation magnetization were measured in the field of 8.6 kOe and temperature region 77–700 K for the samples $\text{MnMe}_\delta\text{Sb}$ (where Me—Mn, Zn, Cu; and $\delta = 0.1; 0.2$).

The temperature dependence of for mono-phase samples is shown at Fig. 2. The comparison of the magnetization curve for $\text{MnZn}_{0.1}\text{Sb}$ and $\text{MnCu}_{0.1}\text{Sb}$ with that for the unsubstituted $\text{Mn}_{1.1}\text{Sb}$ shows that the Curie points for the substituted samples are higher. Namely, they are: $T_C \approx 520$ K for the $\text{Mn}_{1.1}\text{Sb}$, $T_C \approx 570$ K for $\text{Mn}_{1.0}\text{Zn}_{0.1}\text{Sb}$ and it is $T_C \approx 590$ K for $\text{Mn}_{1.0}\text{Cu}_{0.1}\text{Sb}$. This was a bit unexpected result. The possible reason of this effect can be the following. According to Goodenough [7], in the absence of Jahn–Teller distortion the $3d^4$ configuration of Mn^{3+} should lead to ferromagnetic coupling via 135° cation–anion–cation exchange and all the direct metal–metal should be antiferromagnetic. The octahedral (MeI) and bipyramidal (MeII) sites share a common face permitting the MeII cations to interact directly with six neighboring MeI site cations. Thus

population of the MeII sites with excess Mn^{3+} leads to an increase in the anti-ferromagnetic coupling [2] and manifests itself in a reduction in the magnetic ordering temperature and the net magnetization. That is why the magnetic properties of Mn_{1+x}Sb are strongly dependent on interstitial cation concentration x . We suppose that the nonmagnetic Cu or Zn cations substitute for Mn only in MeII sites when Cu or Zn are substituted in small amounts. So they do not inter-

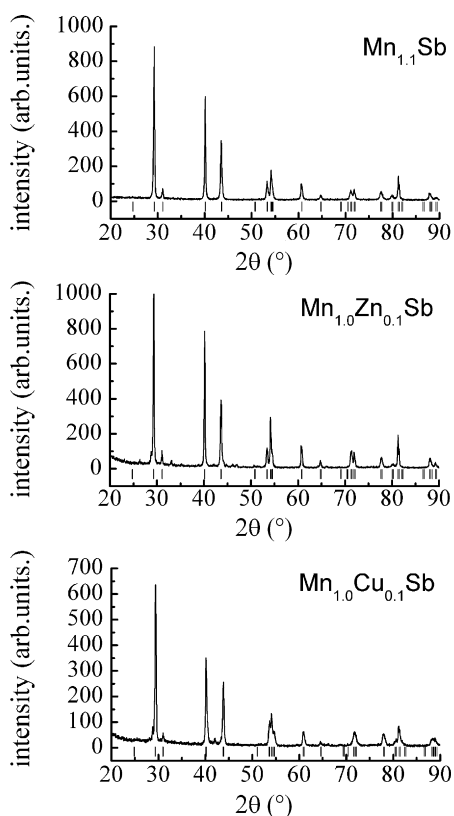


Fig. 1. X-ray analysis results for $\text{Mn}_{1.1}\text{Sb}$, $\text{MnZn}_{0.1}\text{Sb}$ and $\text{MnCu}_{0.1}\text{Sb}$.

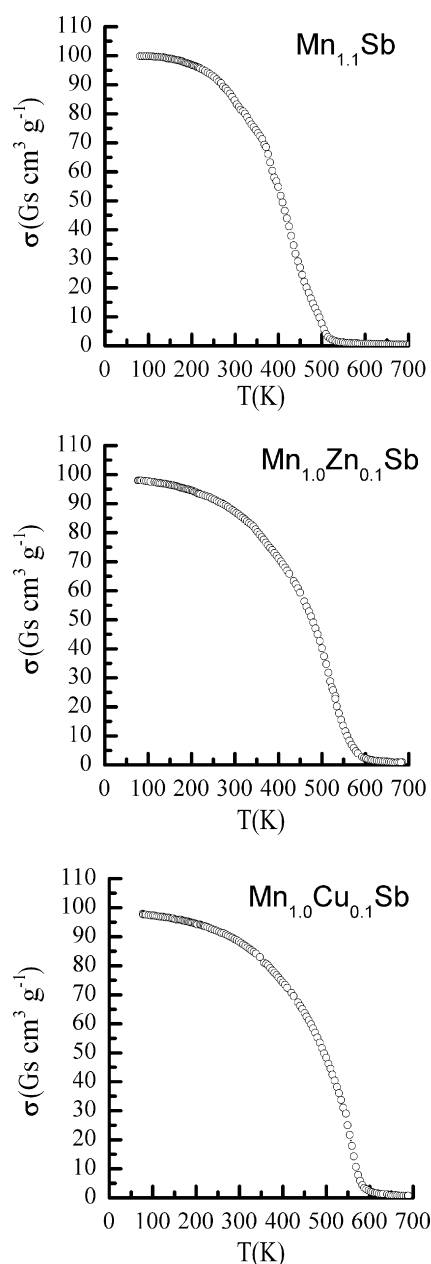


Fig. 2. Magnetic measurement results for $\text{Mn}_{1.1}\text{Sb}$, $\text{MnZn}_{0.1}\text{Sb}$ and $\text{MnCu}_{0.1}\text{Sb}$.

Table 2
The structural characteristics of some MnMeSb (Me—Mn, Zn and Cu) solid solutions with NiAs-type of crystal structure

Sample	Mn _{1,1} Sb	MnZn _{0,1} Sb	MnCu _{0,1} Sb	Mn _{1,2} Sb	Mn _{1,1} Zn _{0,1} Sb	Mn _{1,1} Cu _{0,1} Sb
<i>a</i> (Å)	4.157	4.150	4.133	4.197	4.175	4.164
<i>c</i> (Å)	5.757	5.758	5.770	5.723	5.726	5.775
<i>cla</i>	1.385	1.387	1.396	1.364	1.372	1.387

act magnetically with neighbouring Mn atoms in MeI sites as opposed to the case when the MeII sites are occupied with the Mn atoms either. If to suppose such model of substituting, then the reason of Curie temperature increase for MnZn_{0,1}Sb and MnCu_{0,1}Sb relatively unsubstituted Mn_{1,1}Sb is easily explained. At the same time, it is not completely clear why the saturation magnetization values in the field of 8.6 kOe stay about 100 Gs cm³ g⁻¹ for Mn_{1,1}Sb, MnZn_{0,1}Sb and MnCu_{0,1}Sb.

3. Conclusions

The existence regions of NiAs-type MnSb(Zn) and MnSb(Cu) solid solutions have been determined. Zn and Cu can substitute 10% atomic for Mn.

The Cu or Zn atoms preferable occupy the MeII sites of NiAs-structure if the amount of nonmagnetic substitution not exceed 10% atomic. The preferable occupation of MeII sites by nonmagnetic atom manifests in rising of the Curie temperature of solid solutions relatively unsubstituted alloy.

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