

B8-Type Solid Solutions of Manganese Antimonide and Cu, Zn, Al, or Si

M. BUDZYŃSKI^a, V.I. MITSUİK^{b,*}, Z. SUROWIEC^a AND T.M. TKACHENKA^b

^aInstitute of Physics, UMCS, pl. M. Curie-Skłodowskiej 1, 20-031 Lublin, Poland

^bState Scientific and Production Association “Scientific-Practical Materials Research Centre of National Academy of Sciences of Belarus”, P. Brovki 19, Minsk, 220072 Belarus

The solid solutions with B8-type of crystal structure were prepared in ternary systems MnSb(Zn), MnSb(Cu), MnSb(Al), and MnSb(Si). The ranges of B8 solid solutions existence are limited. The structural and magnetic characteristics were investigated by X-ray powder diffraction, magnetization measurements and the Mössbauer spectroscopy.

DOI: [10.12693/APhysPolA.125.840](https://doi.org/10.12693/APhysPolA.125.840)

PACS: 75.47.Np, 76.80.+y

1. Introduction

The manganese antimonide Mn_{1+x}Sb ($0 \leq x \leq 0.22$) [1] and solid solutions on its basis with the B8-type of crystal structure (space group $P6_3/mmc$) are of practical importance as they manifest the variety of magnetic properties in contrast to their common crystal structure. These structures find practical applications as materials for magneto-optics, temperature-sensitive elements, electrodes for non-aqueous electrochemical cells etc. [2–6].

The purpose of the present work was to produce some new B8-type solid solutions on the basis of manganese antimonide and to study their structural and magnetic properties.

2. Experimental

Various solid solutions with the B8 type of crystal structure in the ternary systems MnSb(Zn), MnSb(Cu), MnSb(Al) and MnSb(Si) were obtained. In order to establish the solubility ranges of Zn, Cu, Al, and Si in MnSb, all the samples were examined by X-ray powder diffraction at room temperature.

The following B8-type solid solutions were prepared using various methods:

(1) The usual heterophase reaction [7] was used to obtain $\text{Mn}_{1.1-x}\text{Cu}_x\text{Sb}$ and $\text{Mn}_{1.1-x}\text{Zn}_x\text{Sb}$ with $x \leq 0.10$;

(2) $\text{Mn}_{1.5-x}\text{Cu}_x\text{Sb}$ ($x \leq 0.30$) and $\text{Mn}_{1.5-x}\text{Zn}_x\text{Sb}$ ($x \leq 0.10$) solid solutions were prepared using high pressure high temperature treatment. This technique ensures an increase in copper content to 30 at.%, but does not influence zinc content [8],

(3) $\text{Mn}_{1.1}\text{Sb}_{1-y}\text{Al}_y$, $y \leq 0.20$ and $\text{Mn}_{1.1}\text{Sb}_{1-y}\text{Si}_y$ with $y \leq 0.10$ were also obtained by method of heterophase reaction [9].

Specific magnetization and saturation magnetization were measured in the field of 8.6 kOe and the temperature range 77 to 700 K for all the samples. The experiment was performed by means of the Faraday method measuring the electromagnetic force which enabled using a small amount of sample. The Curie temperature T_C was determined by a conventional method of extrapolation of the linear part of $\sigma^2(T)$ dependence to T -axes. The accuracy of T_C determination was 5 K.

The Mössbauer measurement was performed at room temperature (293 K). Usual experiment in transmission geometry was carried out with $^{57}\text{Co}(\text{Rh})$ as a gamma resonance source. The Mn content in each sample was partly substituted by the Mössbauer isotope ^{57}Fe when synthesizing (2 at.%). X-ray analysis shows no appreciable difference between the structure of the samples with the Mössbauer isotope addition and those without it. The hyperfine interaction parameters were refined using the Recoil program [10].

TABLE I

The structural and magnetic parameters of B8 type solid solutions on the basis of manganese antimonide.

Sample	a [Å] 293 K	c [Å] 293 K	σ [emu/g] 77 K	T_C [K]
$\text{Mn}_{1.1}\text{Sb}$	4.157	5.757	99.7	520
$\text{MnZn}_{0.1}\text{Sb}$	4.150	5.758	97.9	570
$\text{MnCu}_{0.1}\text{Sb}$	4.133	5.770	97.8	590
$\text{Mn}_{1.2}\text{Sb}$	4.197	5.723	92.9	540
$\text{Mn}_{1.1}\text{Zn}_{0.1}\text{Sb}$	4.175	5.726	90.2	570
$\text{Mn}_{1.1}\text{Cu}_{0.1}\text{Sb}$	4.164	5.775	90.5	580
$\text{Mn}_{1.5}\text{Sb}$	4.281	5.648	26	230
$\text{Mn}_{1.4}\text{Zn}_{0.1}\text{Sb}$	4.302	5.656	27	260
$\text{Mn}_{1.3}\text{Cu}_{0.2}\text{Sb}$	4.236	5.674	44	350
$\text{Mn}_{1.2}\text{Cu}_{0.3}\text{Sb}$	4.243	5.671	38	450
$\text{Mn}_{1.1}\text{Si}_{0.1}\text{Sb}_{0.9}$	4.167	5.742	93	470
$\text{Mn}_{1.1}\text{Al}_{0.1}\text{Sb}_{0.9}$	4.177	5.734	88	465

a , c — lattice parameters, σ — magnetization, T_C — Curie temperature.

*corresponding author; e-mail: mitsiuk@physics.by

TABLE II

Hyperfine interactions parameters at room temperature for B8 type solid solutions on the basis of manganese antimonide.

Sample \ parameters	Sub spectrum	IS [mm/s]	QS [mm/s]	H_{eff} [T]	W [mm/s]	A [%]
Mn _{1.1} Sb	Sextet 1	0.50	0.19	6.1	0.21	74
	Sextet 2	0.55	-0.10	8.2	0.17	26
MnZn _{0.1} Sb	Sextet 1	0.49	0.20	6.1	0.22	49
	Sextet 2	0.53	-0.11	8.0	0.16	51
Mn _{1.05} Cu _{0.05} Sb	Sextet 1	0.44	0.33	6.3	0.33	22
	Sextet 2	0.51	-0.12	7.8	0.15	78
Mn _{1.5} Sb	Dublet	0.41	0.41	-	0.15	100
Mn _{1.4} Zn _{0.1} Sb	Dublet	0.41	0.39	-	0.15	100
Mn _{1.2} Cu _{0.3} Sb	Sextet 1	0.32	-0.10	1.8	0.14	14.7
	Sextet 2	0.44	-0.09	4.8	0.22	47.4
	Dublet1	0.39	0.55	-	0.19	21.3
	Dublet2	0.32	0.13	-	0.16	16.6
Mn _{1.1} Si _{0.1} Sb _{0.9}	Sextet 1	0.39	-0.28	5.8	0.19(fix)	3
	Sextet 2	0.42	-0.20	8.5	0.19(fix)	17.5
	Dublet1	0.14	0.35	-	0.17(fix)	79.5
Mn _{1.1} Al _{0.1} Sb _{0.9}	Sextet 1	0.47	-0.30	5.1	0.19(fix)	2.5
	Sextet 2	0.78	-0.24	6.3	0.19(fix)	61.5
	Dublet1	0.34	0.46	-	0.17(fix)	36

IS — Isomer Shift value relative to the Co/Rh source,
 QS — Quadrupole Splitting, H_{eff} — Hyperfine magnetic field
 W — line width, A — relative subspectrum area

The structural and magnetic parameters for the solid solutions are collected in Table I.

The Mossbauer ^{57}Fe parameters for the solid solutions at room temperature are collected in Table II.

3. Results and discussion

The metal atoms in the B8 type compounds occupy two types of crystal positions: octahedral and trigonal-bipyramidal ones. There was some ambiguity in the literature about the magnetic moment of metal atoms in trigonal-bipyramidal positions in Mn_{1+x}Sb. In [11] no magnetic moment had been obtained for those metal atoms. In [12, 13] it was shown that the metal atoms in both types of structural position have the magnetic moments of different values. In our Mössbauer study [14], contrary to [15], we used the two sextet model in magnetic spectra fitting; that provide the best fitting to experimental results. According to [12], the magnetic moment of Mn-atom in octahedral position in Mn_{1.10}Sb is $3.6 \mu_B$ while it is $3.0 \mu_B$ for the trigonal-bipyramidal Mn atom. That is why we suppose that the subspectrum in each solid solution spectrum characterized by large H_{eff} value corresponds to the Fe atoms located in the regular octahedral positions. The subspectrum with the low H_{eff} value is attributed to the metal atoms located in the trigonal-bipyramidal sites. Our Mössbauer studies on Mn_{1+x}Sb and solid solutions on its basis confirms the fact that there are two types of non-equivalent magnetic positions of metal atoms.

On the basis of the Mössbauer and magnetic data it was concluded that the solution of Cu or Zn in the manganese antimonide up to 10 at.% of component leads to some redistribution of the metal atoms between the two types of structurally non-equivalent positions.

Namely, the Cu or Zn atoms preferably incorporate in the trigonal-bipyramidal sublattice. Such type of substitution explains why the Curie temperature for the parent Mn_{1.1}Sb (Table I) is a bit lower than that for the MnZn_{0.1}Sb and MnCu_{0.1}Sb. We supposed that the metal atoms in each sublattice (octahedral or trigonal-bipyramidal) interact in a ferromagnetic manner, while the interaction between the two different sublattices carries the antiferromagnetic type. If nonmagnetic Cu or Zn atoms occupy only the trigonal-bipyramidal sites, then they do not interact in antiferromagnetic way with neighbouring octahedral Mn atoms. In the parent Mn_{1.1}Sb, the Mn atoms occupy both octahedral and trigonal-bipyramidal sites.

It was found that the hyperfine magnetic field value at ^{57}Fe in Mn(Zn)Sb and Mn(Cu)Sb solid solutions depends significantly on the preparation procedure. The field value is considerably lower for the solid solutions prepared at high pressure than that in the alloys prepared by conventional melting, which attests the marked weakening of interatomic magnetic interactions. This weakening is contributed by the thermodynamically non-equilibrium state of the alloys processed at high pressure and temperature.

The Mössbauer spectroscopy results on the Mn_{1.1}Sb_{1-y}Al_y ($0 < y \leq 0.2$) and Mn_{1.1}Si_{0.1}Sb_{0.9} confirm that the Si or Al atoms replace the Sb ones [11]. These solid solutions contain Fe in three distinct magnetic states because of different local environment of the iron atoms. Two of them are similar to those in MnSb with Zn or Cu, but in MnSb with Al or Si there are Fe atoms in nonmagnetic state either. The reason seems to be as following. The magnetic interactions between metal atoms (Mn or Fe) in different structural positions are realized as indirect exchange between metal atoms via Sb. As some of Sb atoms are substituted for Al or Si, the magnetic interaction at the metal atom closest to this metalloid atom is blocked [9].

4. Summary

A series of new solid solutions with varied magnetic properties were obtained on the basis of manganese antimonide with the B8-type of crystal structure: Mn_{1.1-x}Cu_xSb and Mn_{1.1-x}Zn_xSb ($x \leq 0.10$), Mn_{1.5-x}Cu_xSb ($x \leq 0.30$) and Mn_{1.5-x}Zn_xSb ($x \leq 0.10$), Mn_{1.1}Sb_{1-y}Al_y ($y \leq 0.20$) and Mn_{1.1}Sb_{1-y}Si_y ($y \leq 0.10$). The structural, magnetic and Mössbauer measurements were performed. The sum of experimental data showed that the magnetic characteristics of the parent MnSb are affected by Cu or Zn substitutions more appreciably than by Al or Si. The Cu and Zn atoms preferably replace the Mn atoms in the trigonal-bipyramidal positions of B8 structure, while the Si or Al atoms replace the Sb ones.

Acknowledgments

The work was supported in part by grant No. T13K-003 (Belarusian Republican Foundation for Fundamental Research).

References

- [1] I. Teramoto, A.M.J.G. Van Run, *J. Phys. Chem. Solids* **29**, 347 (1968).
- [2] M.M. Thackeray, J.T. Vaughey, C.S. Johnson, A.J. Kropf, R. Benedek, L.M.L. Fransson, *J. Power Sources* **113**, 124 (2003).
- [3] C.M. Ionica, P.E. Lippens, J.O. Fourcade, J.-C. Jumas, *J. Power Sources* **146**, 478 (2005).
- [4] J.T. Vaughey, L.M.L. Fransson, M.M. Thackeray, Negative electrodes for lithium cells and batteries, United States Patent 6,855,460 (2005). techportal.eere.energy.gov/patent.do/ID=14047.
- [5] G.C Han, C.K Ong, T.Y.F Liew, *J. Magn. Magn. Mater.* **199**, 233 (1992).
- [6] V.I. Mitsiuk, V.M. Ryzhkovskii, T.M. Tkachenka, Magnetic material, Patent BY No. 11937 (2009).
- [7] V.I. Mitsiuk, V.M. Ryzhkovskii, T.M. Tkachenka, *J. Alloys Comp.* **467**, 268 (2009).
- [8] M. Budzyński, V.I. Mitsiuk, V.V. Ryzhkovskii, Z. Surowiec, T.M. Tkachenka, *Inorg. Mater.* **46**, 1067 (2010).
- [9] M. Budzyński, V.I. Mitsiuk, V.V. Ryzhkovskii, Z. Surowiec, T.M. Tkachenka, *Inorg. Mater.* **49**, 105 (2013).
- [10] K. Lagarec, D.G. Rancourt, *Nucl. Instrum. Meth. B* **129**, 266 (1997).
- [11] Y. Yamaguchi, H. Watanabe, T. Suzuki, *J. Phys. Soc. Jpn.* **45**, 703 (1976).
- [12] J. Bouwma, C.F. Van Bruggen, C. Haas, B. van Laar, *J. Phys. C (France)* **32**, 1 (1971).
- [13] J. Nakamura, Y. Kobayashi, K. Asai, N. Yamada, F. Ambe, in: *RIKEN Review No 16: Focused on Nuclear Probes in Physics, Chemistry and Biology* (1997), p. 31.
- [14] V.I. Mitsiuk, V.M. Ryzhkovskii, T.M. Tkachenka, *AIP Conf. Proc.* **1070**, 64 (2008).
- [15] C. Blaauw, G.R. MacKay, W. Leiper, *J. Phys. C: Solid State Phys.* **10**, 5071 (1977).