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Solid solutions $ZrNi_{1-x}M_xSn$ (M = Cr, Mn, Cu) and their electrical and magnetic properties

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Abstract

Solid solutions of $ZrNi_{1-x}M_xSn$ (M = Cr, Mn, Cu) were obtained on the basis of the ZrNiSn semiconducting compound with MgAgAs structure type. X-ray analysis was used to define the stability range of solid solutions: x = 0.4, 0.5, and 0.1 for Cr, Mn, and Cu, respectively. The temperature dependence of resistivity changes from semiconducting to metallic type with increasing x; the thermopower remains negative for all investigated samples. The temperature dependence of the magnetic susceptibility for $ZrNi_{1-x}Mn_xSn$ and $ZrNi_{1-x}Cr_xSn$ can be described approximately by Curie-Weiss law, and the onset of a spontaneous magnetization occurs for small quantities of Mn or Cr. Solid solutions with Cu are paramagnetic. © 1997 Elsevier Science S.A.

Keywords: Solid solutions; Stannides; Semiconductor; Thermopower; Electrical resistivity; Magnetic susceptibility

1. Introduction

The large group of intermetallics with the MgAgAs structure type is characterized by a rich variety of magnetic and transport properties — from metallic to semiconducting ones [1,2]. In particular, MNiSn (M = Ti, Zr, Hf) stannides are semiconductors with narrow bands [1,3–5]. The stability of these phases, in general, is determined by the electron concentration (EC) factor. EC factor in this case is equal to 8 electrons per formula unit noting that Zr and Sn atoms give 4 electrons to the valence bands, and Ni, the 3d band of which is filled, gives nearly no bonding electrons. Doping MNiSn compounds with some elements that cause EC deviations from 8 electrons per formula unit while retaining the same crystal structure can modify dramatically the transport properties of these compounds [2,6]. For example, the properties of $ZrNi_{1-x}Co_xSn$ ($x_{max} = 0.5$) change gradually from semiconducting to metallic ones. The replacement of a small Ni quantity leads to a change of the thermopower from negative in ZrNiSn to positive (+150 to +200 $\mu V/K$ at 300 K for x = 0.05–0.15) but the magnetic susceptibility stays like that for ZrNiSn which is a Pauli paramagnet. Fe cannot replace Ni in ZrNiSn. Magnetic and electrical properties of the $TiCo_xNi_{1-x}Sn$ have been studied [7], cross-over from metal to semiconductor and from non-magnetic semiconductor to itinerant ferromagnet were observed in the series.

The ZrNiSn compound can be a good thermoelectric material [2]. We carry out a systematic study of solid solutions on the ZrNiSn basis with the aim first to find out if $ZrNi_{1-x}Mn_xSn$ and $ZrNi_{1-x}Cr_xSn$ solid solutions can be formed, then to obtain samples with

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Table 1
The characteristics of $ZrNi_{1-x}M_xSn$ solid solution alloys (M = Cr, Mn, Cu). Resistivity and thermopower values are room temperature data. Effective moments are given per Cr or per Mn atom

Alloy composition	a (nm)	ρ ($\mu\Omega$.m)	α (μV/K)	Θ_p (K)	μ_{eff} (μ_B)
$ZrNi_{0.95}Cr_{0.05}Sn$	0.6094(1)	25.0	−192	111	4.07(2)
$ZrNi_{0.90}Cr_{0.10}Sn$	0.60952(9)	35.2	−66	98	1.221(5)
$ZrNi_{0.80}Cr_{0.20}Sn$	0.60955(6)	8.3	−24	135	1.65(3)
$ZrNi_{0.75}Cr_{0.25}Sn$	0.60968(6)	5.1	−15	Pauli paramagnet	
$ZrNi_{0.70}Cr_{0.30}Sn$	0.6097(1)	3.3	−5.9	Pauli paramagnet	
$ZrNi_{0.60}Cr_{0.40}Sn$	0.60981(7)	2.3	−4.5	Pauli paramagnet	
$ZrNi_{0.95}Cu_{0.05}Sn$	0.6102(3)	5.2	−78	Pauli paramagnet	
$ZrNi_{0.90}Cu_{0.10}Sn$	0.6109(2)	3.7	−58	Pauli paramagnet	
$ZrNi_{0.95}Mn_{0.05}Sn$	0.6093(1)	84.5	−230	151	4.43(1)
$ZrNi_{0.90}Mn_{0.10}Sn$	0.60944(8)	68.0	−138	118	4.08(2)
$ZrNi_{0.80}Mn_{0.20}Sn$	0.60953(9)	26.0	−118	78	3.38(2)
$ZrNi_{0.75}Mn_{0.25}Sn$	0.6096(1)	31.2	−46	20	3.88(2)
$ZrNi_{0.70}Mn_{0.30}Sn$	0.60968(6)	—	−457	50	3.83(1)
$ZrNi_{0.60}Mn_{0.40}Sn$	0.60966(7)	22.6	−32	−53	3.90(1)
$ZrNi_{0.50}Mn_{0.50}Sn$	0.60971(9)	15.3	−13	−12	3.86(2)

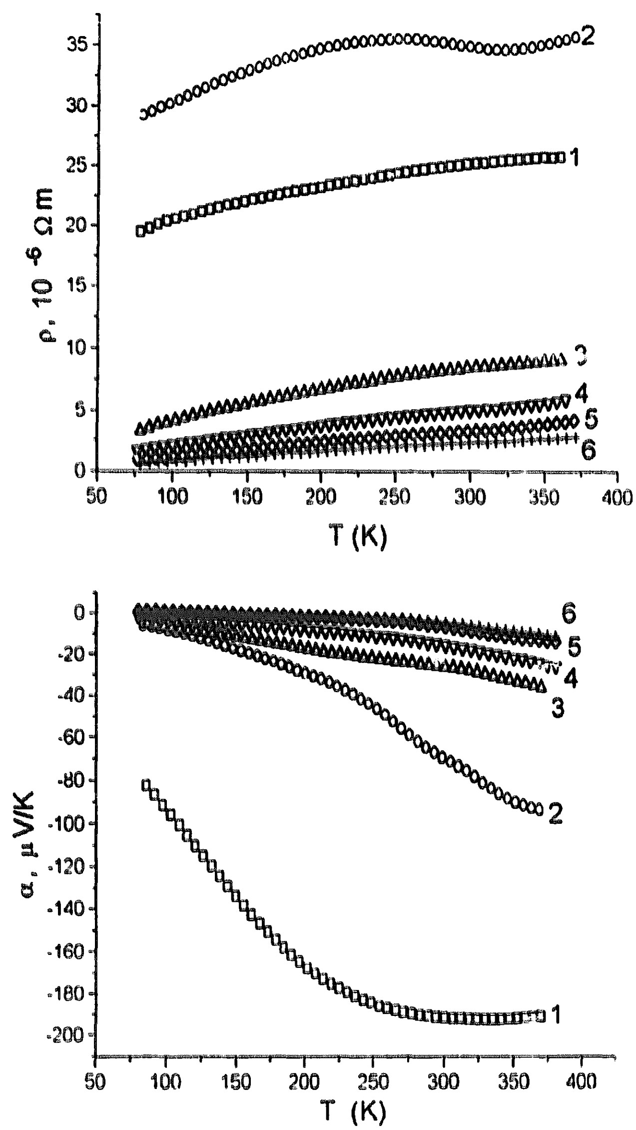

Fig. 1. Resistivity (ρ) and thermopower (α) as functions of temperature for $ZrNi_{1-x}Cr_xSn$ solid solutions: (1) x = 0.05, (2) x = 0.10, (3) x = 0.2, (4) x = 0.25, (5) x = 0.3, (6) x = 0.4.

high thermopower of the n- and p-types and low values of resistivity simultaneously. As the Mn and Cr atoms often bear localized magnetic moments in the intermetallic compounds with transition elements it is interesting to study the magnetic properties of possible solid solutions.

2. Experimental conditions

Samples of nominal compositions were prepared by arc-melting of the pure metals (purity of the constituents is better than 99.9%) using a tungsten electrode under a high-purity argon atmosphere. The alloys were homogenized by annealing at 1070 K for 720 h in evacuated quartz tubes. The phase purity of the samples was checked by X-ray analysis. The electrical resistivity (ρ) and differential thermopower (α) relative to copper were measured as described in [8]. The magnetization (σ) was measured using a vibrating sample magnetometer in magnetic fields up to 0.9 MA/m, whereas the magnetic susceptibility (χ) was measured using the Faraday balance technique.

3. Results and discussion

Doping the ZrNiSn compound (structure type MgAgAs, space group $F\bar{4}3m$, a = 0.6099 nm [1]) with Cr, Mn, and Cu gives rise to solid solutions. The homogeneity region of these solid solutions depends on the doping elements. Solid solutions $ZrNi_{1-x}Mn_xSn$ and $ZrNi_{1-x}Cr_xSn$ exist up to x = 0.5 and x = 0.4, respectively. The solid solution for $ZrNi_{1-x}Cu_xSn$ has a considerably smaller existence range (x = 0.1). The lattice parameters of these solid solutions do not change significantly (Table 1); this

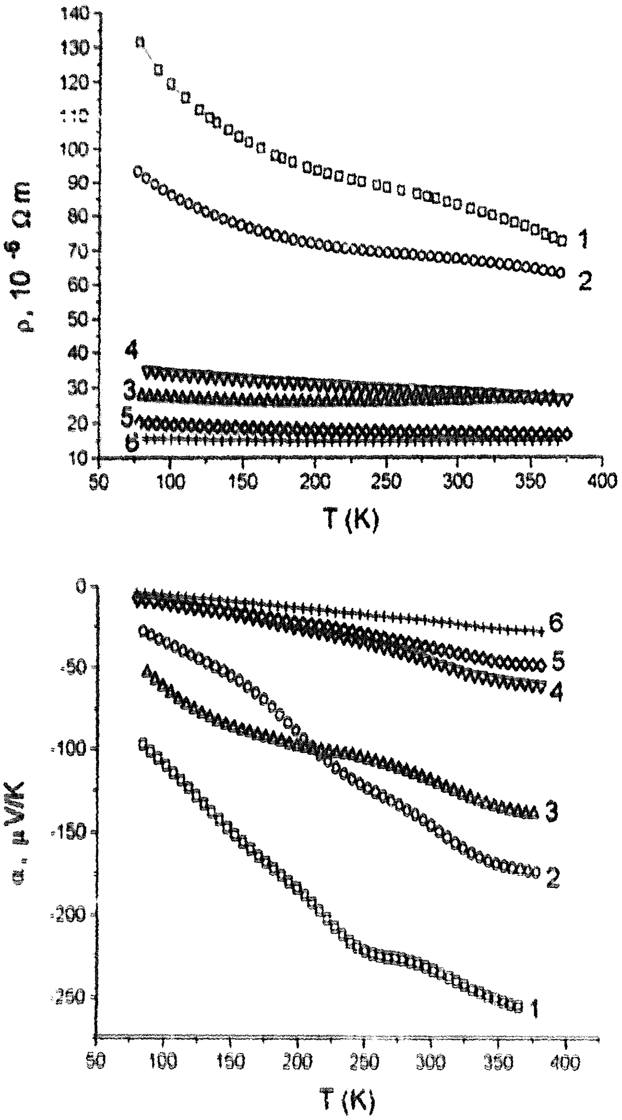

Fig. 2. Resistivity (ρ) and thermopower (α) as functions of temperature for $ZrNi_{1-x}Mn_xSn$ solid solutions: (1) $x = 0.05$, (2) $x = 0.10$, (3) $x = 0.2$, (4) $x = 0.25$, (5) $x = 0.4$, (6) $x = 0.5$.

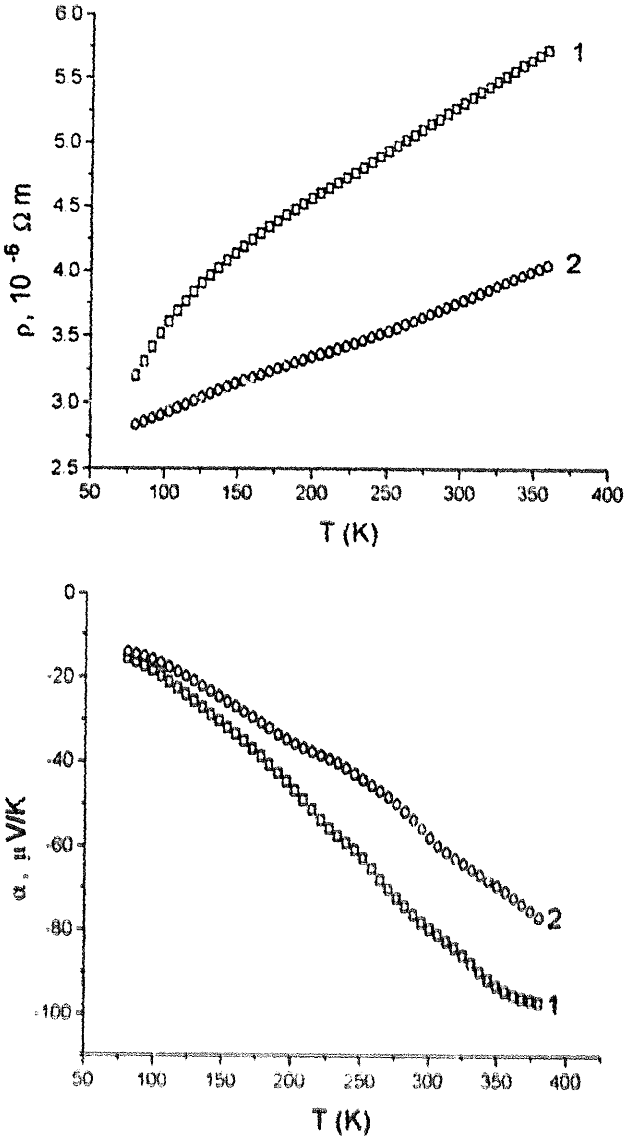

Fig. 3. Resistivity (ρ) and thermopower (α) as functions of temperature for $ZrNi_{1-x}Cu_xSn$ solid solutions: (1) $x = 0.05$, (2) $x = 0.10$.

fact shows that Cr, Mn, and Cu atoms replace Ni. If Cr, Mn, and Cu atoms replaced Zr or Sn or filled vacancies of the ZrNiSn structure, the a parameter would be changed considerably because there is a big difference of atomic radii between Ni and Zr or Sn, whereas the difference between Ni and the doping elements is not significant.

The temperature dependencies of ρ and α are presented in Figs. 1–3. The resistivity of $ZrNi_{1-x}Cu_xSn$ solid solutions is characterized by a metallic type and has the lowest values of all investigated series. This resistivity decreases when Cu concentration increases but the thermopower changes more slightly. A Cu atom replacing Ni in the compound brings one electron more and thus EC deviates from 8. Donor states appear in the gap of ZrNiSn and the resistivity decreases. For larger Cu concentration, these states overlap and merge into the conduction band, which begins to be filled. It can be speculated that $ZrNi_{1-x}Cu_xSn$ solid solutions have an electronic structure like semimetals, the thermopower of which is often high (for instance solid solutions between Bi and Sb).

The $\rho(T)$ dependence for $ZrNi_{1-x}Cr_xSn$ solid solutions is similar to the $\rho(T)$ plots of copper-doped alloys but the resistivity values are approximately one order of magnitude larger than for copper alloys. Mn substitution of Ni in the ZrNiSn compound leads to a gradual change of $\rho(T)$ from semiconducting to semimetallic types. Contrary to Co solid solutions, all the solid solutions investigated in this study have negative values of the thermopower (Figs. 1–3), as well when adding as removing 3d electrons. The thermopower increases in absolute value with increasing temperature and decreases in magnitude with rising concentration of doping components.

A dependence of the magnetic susceptibility on magnetic field (tendency to saturate the magnetization) was observed in $ZrNi_{1-x}Mn_xSn$ and $ZrNi_{1-x}Cr_xSn$ alloys. This $\chi(H)$ dependence is pronounced for small Mn concentration and becomes nearly negligible for the maximum concentration of doping components. The same $\chi(H)$ dependence is observed for the Cr-containing alloys with $x = 0.05$–0.2. At higher Cr content (0.25–0.40), the alloys become Pauli paramagnets. All Mn alloys, and $ZrNi_{1-x}Cr_xSn$ with $x = 0.05$–0.2, can be approximately described by a Curie-Weiss law at high enough temperatures, the magnitudes of effective magnetic moments and paramagnetic Curie points are given in Table 1. $ZrNi_{1-x}Cu_xSn$ solid solutions have the smallest χ values ($\sim 10^{-8}$ emu/g).

We think that the influence of Mn and Cr on the electric properties of ZrNiSn is different from that of Cu and Co (Fe does not substitute to Ni). As said before, Cu atoms raise the EC. Co atoms have in the $ZrNi_{1-x}Co_xSn$ an electronic structure close to $3d^{10}$ with a filled 3d band, as shown by the Pauli paramagnetism of $ZrNi_{1-x}Co_xSn$. In this case the electron concentration diminishes and holes appear in the electron structure. Contrary to the case of Cu which gives up one $4s^1$ peripheral electron to the conduction band, Co atoms fill their 3d shell leaving holes in the band (this is shown by the positive thermopower). An Fe atom would change the EC in such a way that the solid solution cannot exist.

The high solubility of Mn and Cr in ZrNiSn and the onset of a magnetic phase at low temperatures, the amount of which diminishes with increasing Mn or Cr content, indicates another mechanism of atomic interactions in these solid solutions. We may suppose that the electron states of Mn and Cr are localized for a small doping rate of these elements. In that case Mn forms magnetic moments with overall ferromagnetic interactions, and the 3d shell does not contribute (or gives a weak contribution) to bonding electrons. The high value of ρ and α confirms that there is no filling of the 3d shell of Mn by the other valence electrons, otherwise α should be positive (as for Co). However, as the Mn content rises, the hybridization with other electrons should increase, a part of electrons will be shared with the conduction band, modifying the effective electron concentration EC, and the localized moments can disappear, which is revealed by the disappearance of the ferromagnetic magnetization as x rises.

As Mn atoms replace the Ni atoms statistically, a spin glass behavior is probable. The same feature may occur through the replacement of Ni by Cr, and solid solutions have properties similar to those obtained with Mn. Apparently, the Cr valence electrons are more delocalised than Mn electrons. That leads to Pauli paramagnetism of Cr alloys with $x = 0.25$–0.4 and to a smaller value of the resistivity. It can be speculated that the magnetic behavior of $ZrNi_{1-x}Cr_xSn$ can be as complex as that for semimagnetic semiconductors which show magnetic diagrams with transitions from paramagnetic, spin glass to ferromagnetic behavior as a function of the concentration of magnetic atoms [9].

$\chi(H)$ dependencies are usually observed when inhomogeneous magnetic microregions appear in the narrow-gap semiconductors highly doped by magnetic elements [10]. The auto-localization of the charge carriers becomes possible into these magnetic microregions. When temperature is increasing, these inhomogeneous states are destroyed and transition to the metallic state of the conductivity can be observed. The increase in magnetic impurity concentration (Mn or Cr) results in the reduction of the localization, thus to an increased conductivity, which explains the metallization of conductivity in these solutions.

4. Conclusion

The synthesis of the solid solutions $ZrNi_{1-x}M_xSn$ (Cr, Mn, Co, Cu) gave us a possibility to investigate the influence of Ni substitutions in ZrNiSn. Co and Cu, which are adjacent neighbours of Ni in the period, replace the Ni atoms changing the electronic concentration and this change determines the region of solubility. No solid solution was observed for Fe. Small concentrations of Mn or Cr atoms do not change the bonding electron concentration EC as a consequence of the localization of 3d electrons. When increasing further the Cr or Mn content, 3d electrons start to delocalize and hybridize with the conduction band, resulting in a metallic or semimetallic state. Measurements of magnetic and electrical properties at low temperatures and under high magnetic fields are in progress.

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