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Synthesis, crystal structure and physical properties of ZrNiSn semiconductor doped with Mn

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Abstract

The resistivity, thermopower, dc magnetic susceptibility and electron paramagnetic resonance (EPR) spectra of $ZrNi_{1-x}Mn_xSn$ solid solution with low ($0.001 \leq x \leq 0.05$) Mn concentration were investigated in the 78–400 K temperature range. Polycrystalline samples of the $ZrNi_{1-x}Mn_xSn$ compounds were prepared by arc-melting of the pure metals. Quantitative atomic emission spectroscopy confirmed the appropriate Mn contents in all alloys. The lattice parameters of the $ZrNi_{1-x}Mn_xSn$ compounds with different Mn concentration are almost unchanged. Magnetic susceptibility shows the linear dependence versus inverse magnetic field for all samples, what is evidence for the magnetic interactions in the $ZrNi_{1-x}Mn_xSn$ compounds. The temperature dependence of magnetic susceptibility for the compounds with $0.005 \leq x \leq 0.05$ can be described approximately by a Curie–Weiss law. The results of static magnetic measurements were confirmed by EPR technique. The broad line of I type belongs to Mn^{2+} ions in the Ni-sites in crystal lattice coupled by magnetic dipolar interaction. The narrow line of II type is interpreted as an EPR spectrum of exchange-coupled pairs or clusters of more than two Mn^{2+} ions. The unusual magnetic properties and the features of dipolar and exchange interaction of the Mn^{2+} ions in the lattice of $ZrNi_{1-x}Mn_xSn$ solid solution are discussed.

Keywords: Intermetallics; Impurities in semiconductors; Electronic transport, magnetisation; Electron paramagnetic resonance

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1. Introduction

A large group of ternary intermetallic compounds exists with MgAgAs structure type (ST), (space group (SG) $F\bar{4}3m$). Its unusual properties are still attractive, in particular, the MeNiSn ternary stannides (M = Ti,Zr,Hf) with the same ST are narrow gap semiconductors. These are temperature independent Pauli paramagnet [1]. Semiconducting properties of these compounds are retained at valence electron concentration (VEC) values equal to 8 electrons per formula unit [2]. If the VEC changes by substitution of other elements in these compounds, new interesting properties may be observed [3–5].

The $ZrNi_{1-x}Mn_xSn$ and $ZrNi_{1-x}Cr_xSn$ solid solutions based on the semiconducting ZrNiSn ternary compound are characterised by a rich variety of physical properties [1,2]. Electrical and static magnetic properties of the $ZrNi_{1-x}Mn_xSn$ ($0.05 \leq x \leq 0.5$) and $ZrNi_{1-x}Cr_xSn$ ($0.05 \leq x \leq 0.4$) solid solutions were investigated in Ref. [2]. An important feature of these compounds is the onset of magnetic ordering at relatively low Mn or Cr concentration, while large values of the thermopower are obtained. EPR spectroscopy of the $ZrNi_{1-x}Mn_xSn$ solid solution with $0.05 \leq x \leq 0.5$ was first presented in Ref. [6]. The static magnetic properties and EPR spectra of the $ZrNi_{1-x}Cr_xSn$ solid solution ($0.05 \leq x \leq 0.4$) in the 140–300 K temperature range were described in detail in Refs. [7,8]. The precise investigation of dc magnetic susceptibility and EPR spectra in the $ZrNi_{1-x}Cr_xSn$ alloys with $0.005 \leq x \leq 0.25$ and discussion about the nature of magnetic ordering in these compounds are presented in Ref. [9].

In the present work, we study electrical and static magnetic properties of $ZrNi_{1-x}Mn_xSn$ solid solution with low $0.001 \leq x \leq 0.03$ Mn concentration and EPR spectra of the $ZrNi_{1-x}Mn_xSn$ compounds in the whole range of the Mn concentration ($0.001 \leq x \leq 0.5$).

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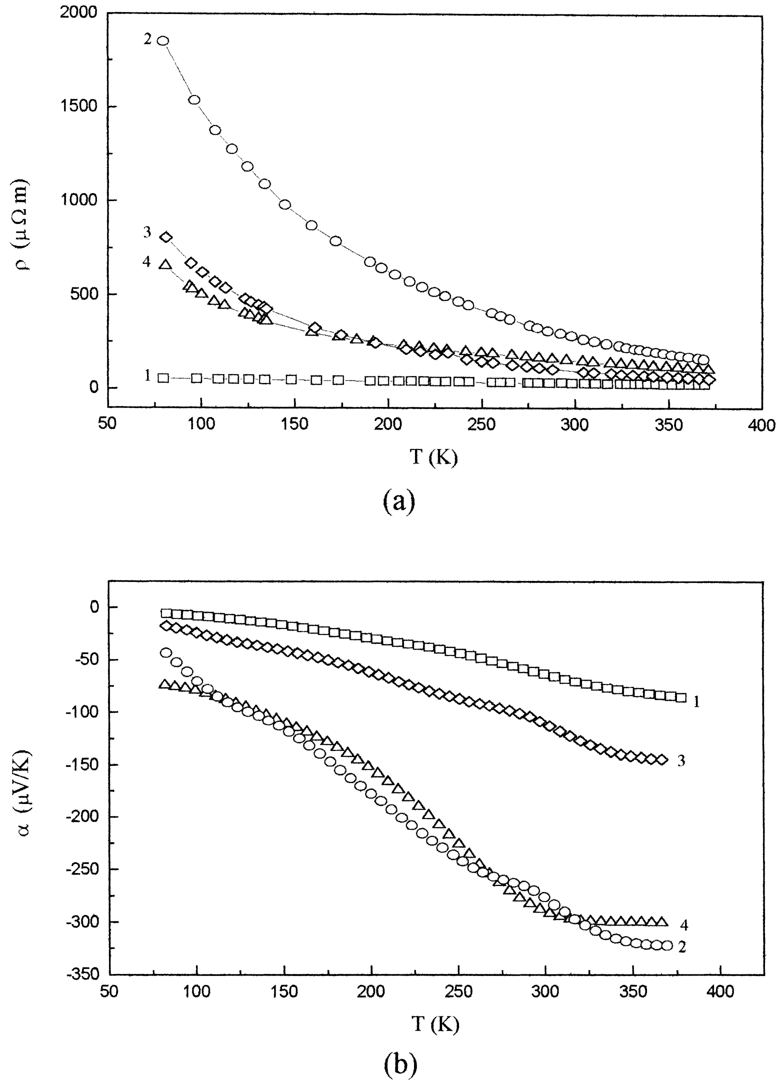
2. Experimental

Samples of nominal compositions were prepared by arc-melting of the pure ingredients (purity of the constituents is better than 99.99 wt.%) using an unconsumable tungsten electrode under a high-purity Ti-gettered argon atmosphere. The ingots were twice re-melted and then homogenized by annealing at 1070 K for 720 h in evacuated quartz tubes. The phase purity of the samples was controlled by X-ray analysis and microscopic metallography examinations. Chemical composition of the $ZrNi_{1-x}Mn_xSn$ alloys with $0.001 \leq x \leq 0.03$ were also controlled by quantitative atomic emission spectral analysis with three standards [10]. For determination of Mn concentration, the nearly distributed analytical lines pair in optical spectra was selected with $\lambda_{Fe} = 2936$ Å and $\lambda_{Mn} = 2939$ Å. The spectral analysis error is less than 5% with respect to the corresponding concentration. The resistivity (ρ) and differential thermopower (α) in relation to copper were measured as described in Ref. [11]. The dependencies of the specific dc magnetic susceptibility (χ) versus magnetic field and temperature were investigated in the 1–10 kG magnetic field range and in the 84–450 K temperature range, respectively, by a conventional Faraday balance technique. The X-band ($\nu \cong 9.3$ GHz) EPR measurements were carried out using RE-1306 and RADIOPAN SE/X-2544 commercial radio frequency spectrometers with 100 kHz magnetic field modulation at temperatures 300 and 77 K. EPR spectra parameters were defined from the experimental spectra through resonance relationships. The microwave frequency in each case was controlled by means of polycrystalline DPPH (diphenylpicrylhydrazyl) g marker ($g = 2.0036 \pm 0.0002$).



(a)

(b)

Fig. 1. Temperature dependencies of resistivity (a) and thermopower (b) for $ZrNi_{1-x}Mn_xSn$ solid solutions. (1) $x = 0.001$; (2) $x = 0.005$; (3) $x = 0.01$, and (4) $x = 0.03$.

3. Results and discussion

The X-ray powder diffraction and microscopic metallography analyses show that all $ZrNi_{1-x}Mn_xSn$ samples ($0.001 \leq x \leq 0.03$) except $ZrNi_{0.999}Mn_{0.001}Sn$ alloys are single phased. The lattice parameter a changes insignificantly ($a = 0.6102(1)$–$0.6104(1)$ nm) when Mn atoms are substituted for Ni in the ZrNiSn compound because of the small difference between the Ni and Mn atomic radii and low Mn concentration. The $ZrNi_{0.999}Mn_{0.001}Sn$ alloy has nearly 5% impurity of $ZrNi_2Sn$ phase with $MnCu_2Al$ ST. Spectroscopical analysis shows a good agreement with the nominal amount of Mn in these alloys.

From $\rho(T)$ measurements (Fig. 1a) it is obvious that a weak substitution of Mn instead of Ni in the ZrNiSn compound does not result in the disappearance of semiconducting properties in this series. Some anomalies in the $\rho(T)$ behavior for low concentrations may be explained by nonstoichiometry or the occurrence of a $ZrNi_2Sn$ impurity with metallic type of $\rho(T)$ dependence in the 78–400 K temperature range [1]. A further increase of Mn concentration in $ZrNi_{1-x}Mn_xSn$ solid solution results in semiconductor–semimetal transition [2]. In Ref. [2], solid solutions were obtained by replacing Ni by Cr, Mn or Cu. ρ strongly decreases with impurity concentration as well as thermopower. The largest thermopower value (-230 $\mu V\,K^{-1}$ at 300 K) was obtained for the lowest concentration (0.05) of Mn. Thus, in the present study, investigations were extended to even lower concentrations. The differential thermopower for all investigated samples is negative, increases with temperature growth (Fig. 1b), and reaches about -300 $\mu V\,K^{-1}$ at 300 K for $x = 0.005$ and 0.03. Unfortunately, the resistivity is still too high, which reduces the thermoelectric factor of merit.

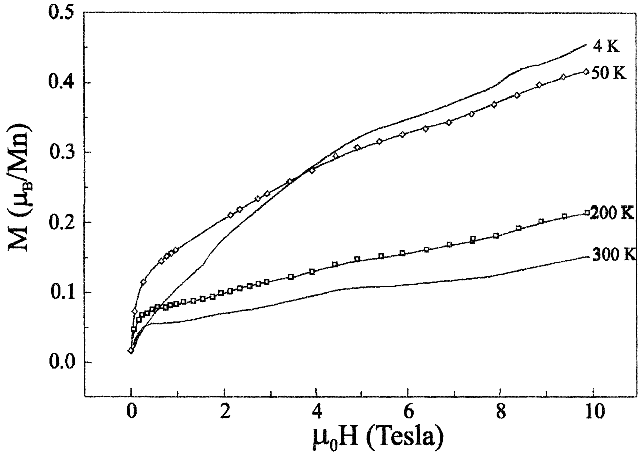


Fig. 3. Magnetization isotherms for $ZrNi_{0.9}Mn_{0.1}Sn$ sample.

In spite of the Mn concentration decrease (down to $x = 0.001$) there is a magnetic field dependence in the $\chi = \chi(1/H)$ plots (as an example, these plots are given in Fig. 2 at various temperatures). This may be evidence of the presence of a magnetic moment and magnetic interactions [12] in all manganese containing alloys ($0.001 \leq x \leq 0.5$). The onset of a magnetic phase at low temperatures is confirmed also on the $ZrNi_{0.9}Mn_{0.1}Sn$ alloy by magnetization measurements in magnetic fields up to 10 T (Fig. 3). The impurity of $ZrNi_2Sn$ phase in $ZrNi_{0.999}Mn_{0.001}Sn$ alloy does not essentially influence the magnetic properties because the $ZrNi_2Sn$ phase is a magnetic field independent Pauli paramagnet [13]. Temperature dependencies of the magnetic susceptibility are approximately described by Curie–Weiss law for higher Mn concentrations [2]. In Fig. 4, the $\chi^{-1}(T)$ dependencies are presented for $ZrNi_{1-x}Mn_xSn$ alloys with low Mn concentration. It can be seen from these plots, that the Curie–Weiss law with appropriate effective magnetic moments equal to 3–3.75

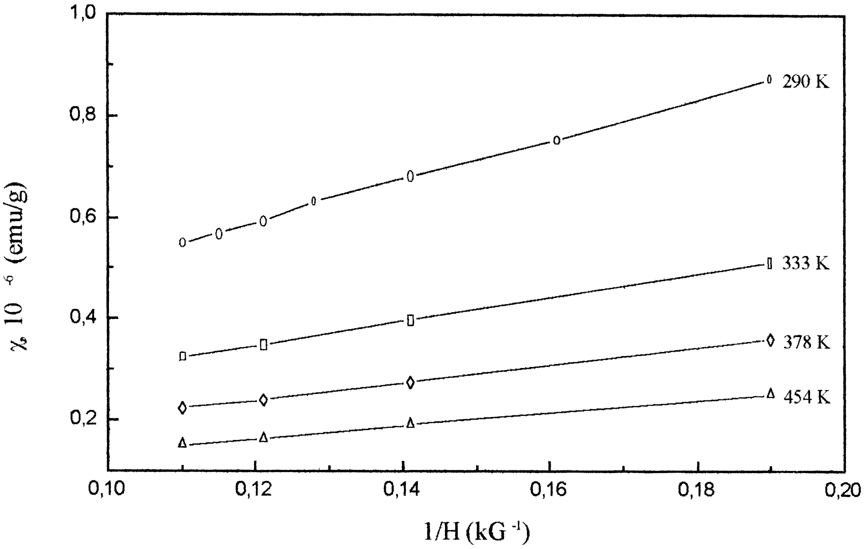


Fig. 2. Variation of specific magnetic susceptibility versus inverse magnetic field ($1/H$) for $ZrNi_{0.995}Mn_{0.005}Sn$ alloy, measured at following temperatures: 290, 333, 378, and 454 K.

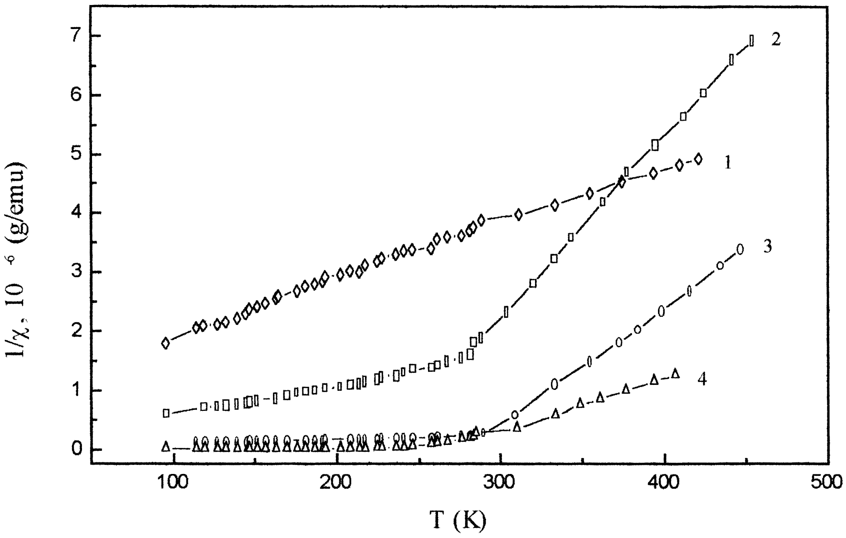


Fig. 4. Plot of inverse value of magnetic susceptibility (χ^{-1}) versus temperature for $ZrNi_{1-x}Mn_xSn$ alloys. (1) $x=0.001$; (2) $x=0.005$; (3) $x=0.01$, and (4) $x=0.03$.

μ_B/Mn takes place for the alloys with $x=0.03$; 0.01; 0.005 above 300 K. Temperature dependence of the $ZrNi_{0.999}Mn_{0.001}Sn$ sample cannot be described by Curie–Weiss law up to 420 K. In our opinion there are either ferromagnetic or spin glass ordering of the Mn moments in all investigated Mn-contained alloys in view of high positive values of magnetic transition temperature. Such ferromagnetic transition was observed in (Pb,Sn,Mn)Te semimagnetic semiconductors with high concentration of the charge carriers [14].

The correct interpretation of unusual magnetic properties of the $ZrNi_{1-x}Mn_xSn$ solid solution needs more detailed investigation using EPR method. A relatively high electrical resistivity of the $ZrNi_{1-x}Mn_xSn$ polycrystalline samples (more than 15.3 $\mu\Omega\,m^{-1}$) [2] allowed us to use a standard EPR technique for the investigation of these

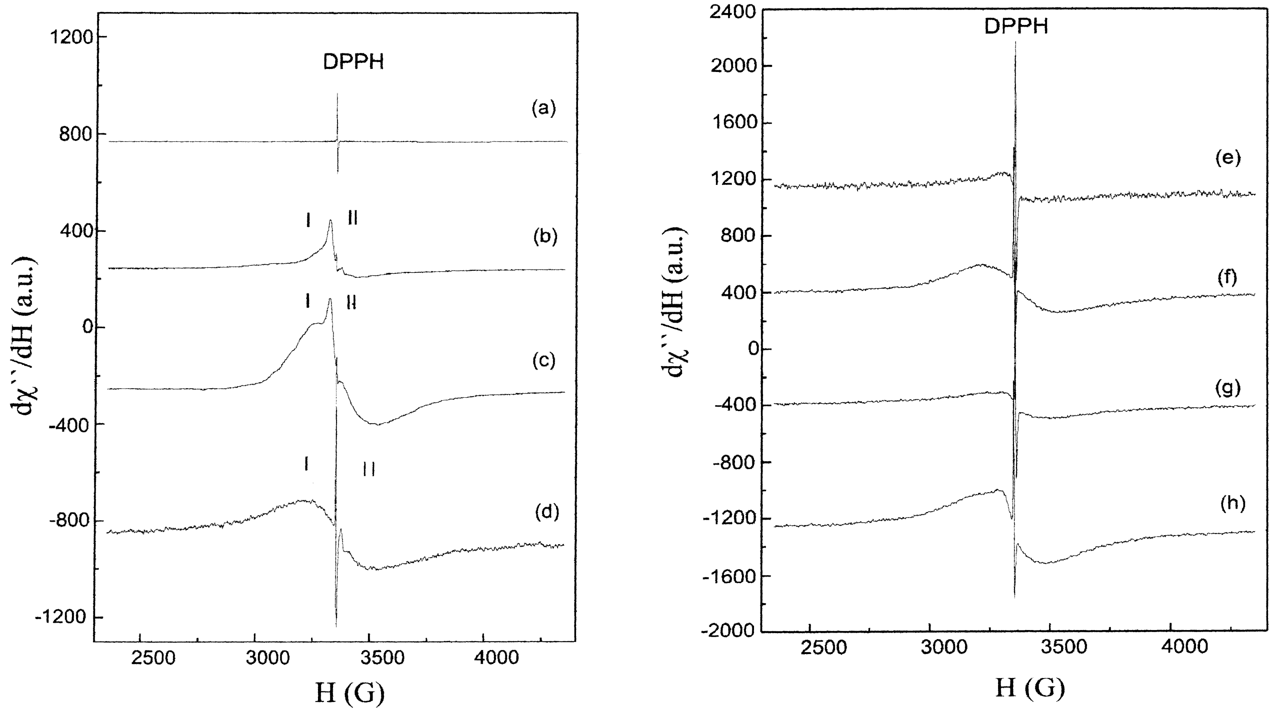


Fig. 5. X-band EPR spectra of polycrystalline $ZrNi_{1-x}Mn_xSn$ samples with high ($0.05\leq x\leq 0.5$) Mn concentration, registered at 300 K. (a) $x=0$; (b) $x=0.05$; (c) $x=0.1$; (d) $x=0.2$; (e) $x=0.25$; (f) $x=0.3$; (g) $x=0.4$, and (h) $x=0.5$.

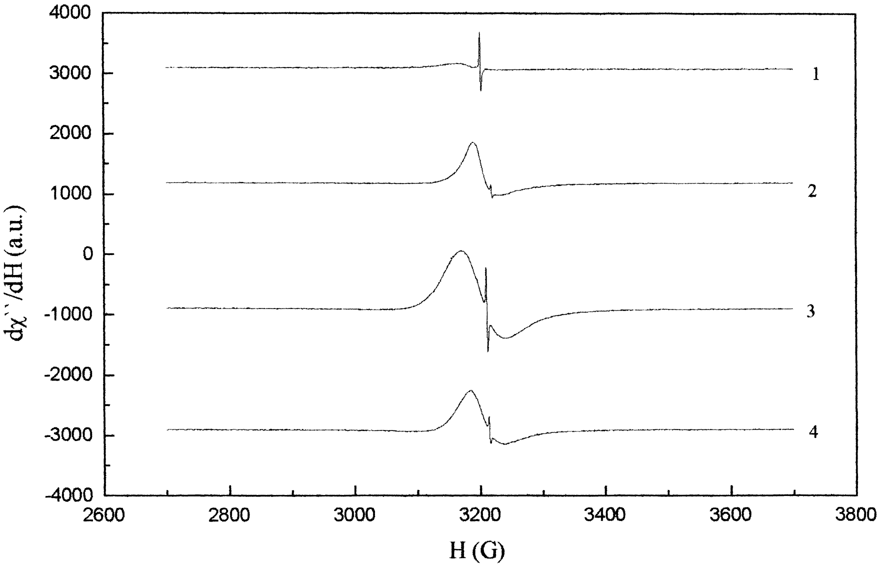


Fig. 6. X-band EPR spectra of polycrystalline $ZrNi_{1-x}Mn_xSn$ samples, with low ($0.001 \leq x \leq 0.03$) Mn concentration, registered at 300 K. (1) $x=0.001$; (2) $x=0.005$; (3) $x=0.01$, and (4) $x=0.03$.

compounds. The X-band EPR spectra of $ZrNi_{1-x}Mn_xSn$ bulk and powdered samples with high ($0.05 \leq x \leq 0.5$) Mn concentration are presented in Fig. 5. It should be noted that in pure ZrNiSn compound no EPR spectra were observed in the 77–300 K temperature range (Fig. 5a). All $ZrNi_{1-x}Mn_xSn$ solid solutions with $0.05 \leq x \leq 0.5$ are characterized by intense EPR spectra in the 3000–3500 G magnetic field range (Fig. 5b–h). EPR spectra of the samples with $x=0.05$, 0.10, 0.20 (Fig. 5b–d) consist of two absorption lines with the following parameters: $g=2.00 \pm 0.02$, $\Delta H_{pp}=500 \pm 20$ G (I type line) and $g=2.01 \pm 0.01$, $\Delta H_{pp}=50 \pm 5$ G (II type line), where g is the g-factor value of EPR line and ΔH_{pp} is the peak-to-peak derivative linewidth. EPR spectra of the samples with $x=0.25$, 0.3, 0.4 consist of one absorption line of I type exclusively (Fig. 5e–g). However, for the $ZrNi_{0.5}Mn_{0.5}Sn$ sample, besides the broad line of I type, a second much narrower ($g \cong 2.00$, $\Delta H_{pp} \cong 250$ G) line was revealed in the EPR spectrum (Fig. 5h). The observed asymmetric Dyson lineshape of the I and II type signals (Fig. 5) is characteristic of metallic-like compounds. Additional inhomogeneous broadening of the absorption lines is caused by polycrystalline forms of the $ZrNi_{1-x}Mn_xSn$ samples, that is characteristic for field-swept ($\nu=$const) EPR spectra in disordered (polycrystalline) compounds [15]. The linewidth, lineshape and intensity of the observed signals are relatively weakly dependent on temperature in the 77–300 K range, but are strongly dependent on the manganese concentration. Both EPR lines of the I and II types belong to the Mn^{2+} ($3d^5$ configuration, $^6S_{5/2}$ free ion ground state). Broad EPR lines of the I type belong to the Mn^{2+} EPR spectrum homogeneously broadened by the magnetic dipolar interaction [16]. The narrow EPR signal (II type line) is interpreted as EPR spectrum of exchange-coupled Mn^{2+} pairs or clusters of more than two Mn^{2+} ions [17] in the lattice of $ZrNi_{1-x}Mn_xSn$ compounds.

EPR spectra of the $ZrNi_{1-x}Mn_xSn$ solid solutions with the lower ($0.001 \leq x \leq 0.03$) Mn concentration ($0.001 \leq x \leq 0.03$) are presented in Fig. 6. It should be noted that even at the lowest Mn concentrations the classical EPR spectrum of the isolated Mn^{2+} ions with well-resolved hyperfine structure, caused by ^{55}Mn isotope (nuclear spin $I=5/2$, natural abundance: 100%) in the ZrNiSn lattice was not observed. As we can see, EPR spectra of the samples with $x=0.001$, 0.005, 0.01, 0.03 consist of single unresolved broad absorption lines of the I type exclusively. Observed lines are also characterised by an inhomogeneous broadened asymmetric Dyson shape (Fig. 6) and are attributed to the Mn^{2+} ions in the Ni sites of lattice coupled by magnetic dipolar interaction. The EPR spectrum of exchange-coupled Mn^{2+} pairs or clusters of more than two Mn^{2+} ions in the $ZrNi_{1-x}Mn_xSn$ samples with low ($0.001 \leq x \leq 0.03$) Mn concentrations was not observed. Thus, the exchange interaction between Mn^{2+} ions reveals in the EPR spectra of $ZrNi_{1-x}Mn_xSn$ samples for $0.05 \leq x \leq 0.2$ (II type line, Fig. 5b–d), whereas for $x < 0.05$ and $x > 0.2$ only I type line is observed (Fig. 5e–h, Fig. 6(1)–(4)). In contrast, in the $ZrNi_{1-x}Cr_xSn$ alloys the increasing chromium concentration results in a reduction of both the localization and the magnetic ordering.

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