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Electronic structure and electric properties of Gd($In_{1-x}Sn_x$)$_3$ compounds

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Results of measurements of the electrical resistivity, crystal and electronic structure of Gd($In_{1-x}Sn_x$)$_3$ compounds are reported. All these compounds crystallize in the cubic $AuCu_3$ type structure. The effect of partial substitution of In by Sn atoms is reflected in a linear increase of the unit cell volume. The temperature dependence of the electrical resistivity ρ strongly depends on the composition. For compounds with $x \geq 0.1$, the $\rho(T)$ behavior, observed at low temperatures, is untypical of metals. The electronic structure of all systems was studied by using X-ray photoelectron spectroscopy. The chemical shift of the 4f Gd peak to higher binding energy with the increase of Sn concentration was detected. The valence band near the Fermi level is dominated by hybridized 5d Gd and 5p In/Sn states.

Key words: *intermetallics; photoelectron spectroscopy; electrical resistivity*

1. Introduction

Intermetallic compounds RSn_3 and RIn_3 and their pseudobinary alloys show many interesting properties such as the presence of various magnetic structures, valence fluctuations and magnetic moment formation. Some of these features are not fully understood, hence the study of a system with R = Gd, which has a half-filled shell, seems to be well-founded. Both $GdIn_3$ and $GdSn_3$ are antiferromagnets with the transition temperatures (T_N) of 45 K and 31 K, respectively, and crystallize in the cubic $AuCu_3$-type of structure (space group *Pmcm*) [1, 2]. The measurements of the magnetic susceptibility for the Gd($Sn_{1-x}In_x$)$_3$ performed by Lin, Yuen et al. [3] exhibited an oscillatory variation of the antiferromagnetic transition temperature T_{N1} across the whole series, as well the appearance of the second magnetic transition T_{N2} at lower temperatures for some In-doped samples. The Mössbauer results [4] have shown that magnetic structure of the system changes from type I antiferromagnetic ordering on the Sn-rich side to type II antiferromagnetic ordering on the very rich In side. For the

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range of intermediate In concentrations, the type I antiferromagnetic or the canted antifferomagnetic ordering state was proposed. The oscillatory behaviour in T_{N1} has been attributed to a band-structure effect arising from the mixing of 5d electrons from the rare-earth ions and the s and p bands of Sn and In.

The aim of this work was to investigate the effect of a partial substitution of In by Sn atoms on the electronic structure, examined with the use of X-ray photoelectron spectroscopy (XPS), as well as the electrical resistivity of the $Gd(In_{1-x}Sn_x)_3$ system.

2. Experimental

Polycrystalline samples of the $Gd(In_{1-x}Sn_x)_3$ system with $x = 0.0, 0.05, 0.10, 0.20, 0.50, 0.80$ and 1.00 were prepared from stoichiometric amounts of the constituent metals by arc melting under argon atmosphere. After melting, the samples were annealed in quartz tubes at 650 °C for 5 days. Phase identification of the alloys was performed by powder X-ray diffraction technique using Siemens D5000 diffractometer at room temperature. All samples had a cubic $AuCu_3$ type of structure. The temperature dependence of the electrical resistivity $\rho(T)$ was measured by means of the standard four-probe technique in the temperature range from 4.2 K to 300 K. The samples were cut with a wire saw to a size of $1 \times 1 \times 5$ mm^3.

The electronic structure was studied by means of X-ray photoelectron spectroscopy. The XPS spectra were obtained with monochromatized AlK_α radiation ($h\omega = 1486.6$ eV) at room temperature using a PHI 700/660 Physical Electronics Spectrometer. The spectra were measured immediately after scraping the surface with diamond file in vacuum of 10^{-10} Torr. The scraping in high vacuum produced clean surfaces, free of oxygen and carbon contamination.

3. Results and discussion

The substitution of In by Sn in the $Gd(In_{1-x}Sn_x)_3$ system caused a linear increase of the lattice parameter a with concentration x in agreement with Vegard's law (Fig. 1). The character of the temperature variation of the electrical resistivity $\rho(T)$ below the Néel temperature (T_N) indicated a strong dependence on x (Fig. 2). For indium rich compounds (with $x = 0.0$ and 0.05), pronounced changes in the slope of the $\rho(T)$ curves at $T_N = 45$ K and 44 K (respectively) were observed, which is typical of metallic systems. The substitution of 10% In by Sn atoms in the system caused essential change in the character of $\rho(T)$ in the low temperature range. For this compound, the $\rho(T)$ curve shows two minima, at 43 K and 13 K. A non-typical dependence of $\rho(T)$, reflected in an increase of the resistivity with decreasing temperature below T_N was observed for the sample with $x = 0.2$. For higher concentrations of Sn, these minima were very weakly visible. According to the Matthiesen rule, the thermal dependence of electrical resistivity is given by the equation:

$$\rho(\mathrm{T}) = \rho_0 + \rho_{\mathrm{ph}}(T) + \rho_{\mathrm{mag}}(T)$$

where the first term represents a residual resistivity, the second the phonon contribution and the third one the spin-disorder contribution which is caused by the scattering of the conduction electrons on 4f moments.

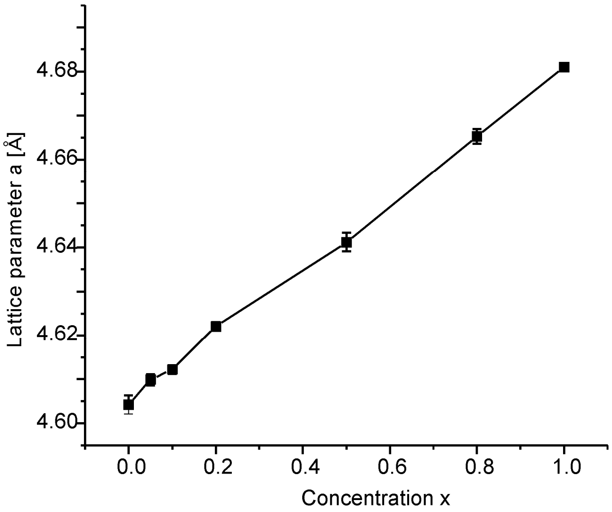

Fig. 1. Lattice parameter *a* versus concentration *x* for the $Gd(In_{1-x}Sn_x)_3$ system

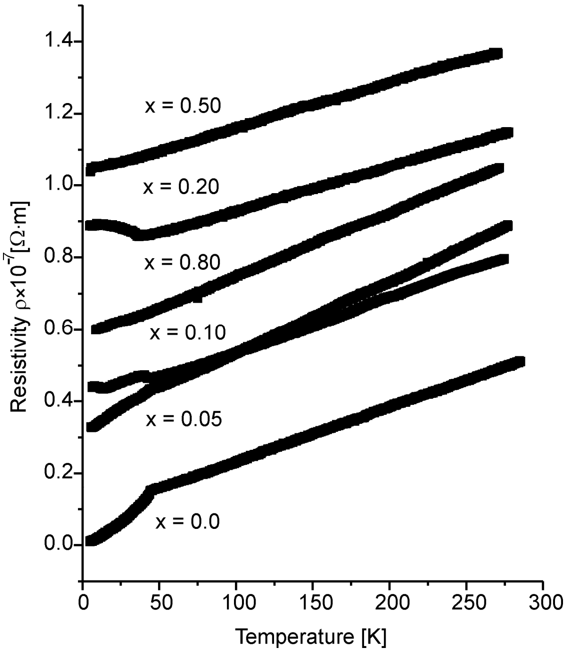

Fig. 2. Temperature dependence of the electrical resistivity of $Gd(In_{1-x}Sn_x)_3$ compounds

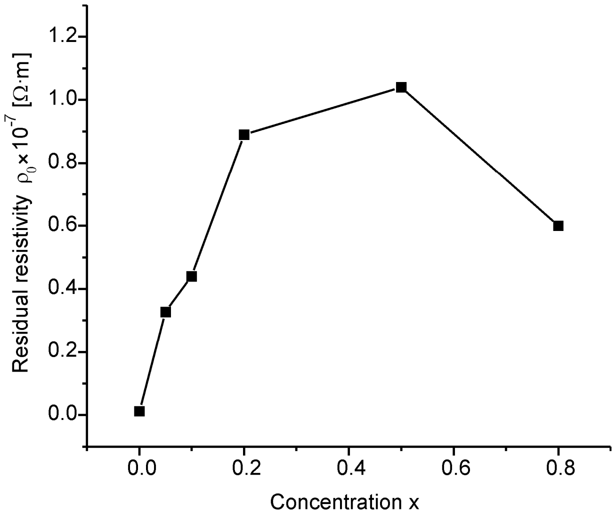

Fig. 3. Residual resistivity $\rho_0(T)$ versus x for the $Gd(In_{1-x}Sn_x)_3$ system

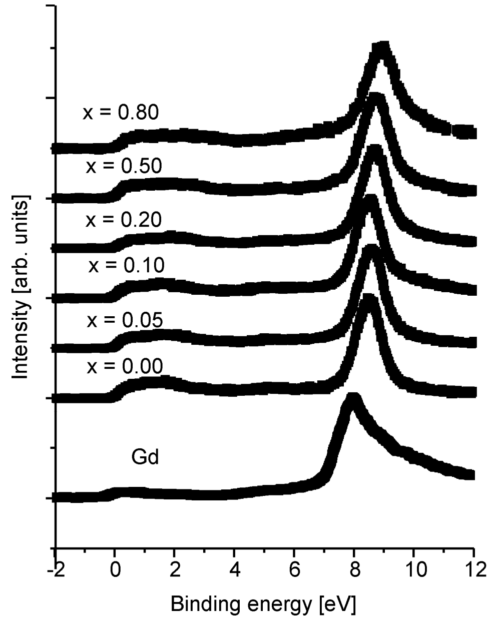

Fig. 4. XPS valence band region of the $Gd(In_{1-x}Sn_x)_3$ system.
The spectrum of pure Gd is included for comparison

In the investigated $Gd(In_{1-x}Sn_x)_3$ system, the residual resistivity ρ_0 increases with x, reaches a maximum around $x = 0.5$ and decreases for Sn-rich compounds (Fig. 3). Such a behaviour of $\rho_0(x)$ can be related to some crystal disorder in the In/Sn sublattice upon the substitution, nevertheless this disorder cannot be the only reason for the non-typical dependence of $\rho(T)$ at low temperatures. The increase of $\rho(T)$ observed below T_N must be connected with some additional mechanism which increases the scattering of conduction electrons. We attribute this anomaly to the complex magnetic structure of these compounds reported in [3, 4].

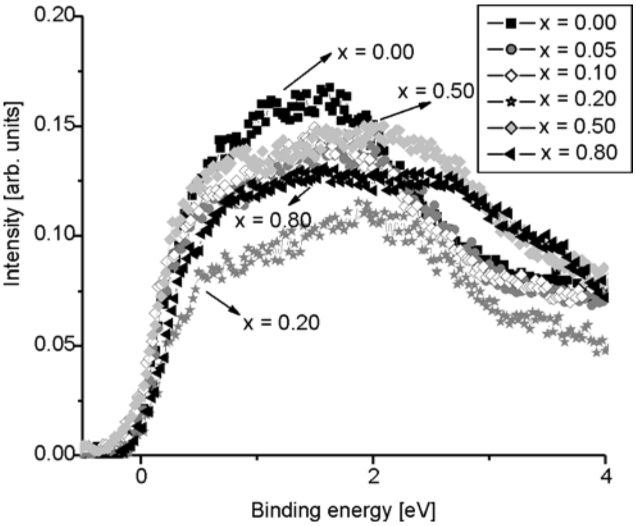

Fig. 5. The XPS spectrum of Gd(In$_{1-x}$Sn$_x$)$_3$ compounds near the Fermi level

Table1. Binding energy of 4f Gd and 4d Gd of the Gd(In$_{1-x}$Sn$_x$)$_3$ system*

Compound	The position of 4f Gd [eV]	The position of 4d Gd [eV]
GdIn$_3$	8.5	140.6
Gd(In$_{0.9}$Sn$_{0.1}$)$_3$	8.6	140.7
Gd(In$_{0.8}$Sn$_{0.2}$)$_3$	8.7	140.8
Gd(In$_{0.5}$Sn$_{0.5}$)$_3$	8.8	141.0
Gd(In$_{0.2}$Sn$_{0.8}$)$_3$	9.0	141.1

* For 4d Gd, the first line of the multiplet was taken into account.

The XPS spectra in the valence band region for Gd(In$_{1-x}$Sn$_x$)$_3$ (x = 0.0, 0.05, 0.1, 0.2, 0.5 and 0.8) are presented in Figs. 4 and 5. All spectra are normalized to the maximum intensity of the 4f Gd peak. The spectrum for pure Gd is added for comparison. In all compounds, the position of 4f Gd photoemission peak is shifted to higher binding energy in relation to that in the metallic Gd. The value of the shift for GdIn$_3$ is about 0.4 eV and is in agreement with the result obtained by Szade et al. [5]. Upon replacing In by Sn atoms, an additional shift of 4f Gd peak is observed. Similar changes in the energy positions were found for 4d Gd levels (not presented here). For analyzing the shift of the 4d Gd level, the first line of the multiplet was taken into account. The values of binding energies of 4f Gd and 4d Gd peaks in all investigated compounds are collected in Table 1. The observed shifts are probably caused by the increase of the environmental potential, resulting from charge transfer from Gd to neighbouring atoms. Gadolinium has lower electronegativity than In and Sn and has a tendency to transfer electrons to other metal sites. The region of binding energy close to the Fermi level E_F (Fig. 5) is characterized by a contribution coming from the 5d Gd, 5p In and 5p Sn states. The observed change in the photoemission intensity, as well as a change of the shape of peaks near E_F with increasing Sn concentration, are caused by the hybridization effect in this energy range, which seems to be consistent with earlier investigations.

Acknowledgements

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