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Electrical transport properties and electronic structure of *R*NiSn compounds (*R* = Y, Gd, Tb, Dy, and Lu)

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A series of RNiSn compounds, where R = Y, Gd, Tb, Dy, and Lu, with the TiNiSi structure type (space group *Pnma*) was synthesized and the electrical transport properties were investigated by means of electrical resistivity and Seebeck coefficient measurements in the temperature range 80-380 K. All of the investigated compounds exhibit metallic-like conductivity. Electronic structure calculations based on the Full Potential Linearized Augmented Plane Wave (FLAPW) method were carried out to obtain the density of states (DOS) for the investigated compounds, from which the electrical properties were explained.

Intermetallics / Crystal structure / Electrical properties / Electronic structure calculations

1. Introduction

Investigations of *R*-Ni-Sn ternary systems (where *R* is a rare-earth metal) have resulted in the discovery of several series of ternary stannides with different structure types, e.g. *R*NiSn (TiNiSi-type), R_6Ni_2Sn (Ho_6Co_2Ga-type), RNi_2Sn_2 ($CaBe_2Ge_2$-type), $RNiSn_2$ ($CeNiSi_2$-type for La through Sm, or $LuNiSn_2$-type for Gd through Lu), RNi_3Sn_2 ($HoNi_{2.6}Ga_{2.4}$-type), $R_9Ni_{24}Sn_{49}$ ($Gd_9Ni_{24}Sn_{49}$-type), R_2NiSn_6 (Lu_2NiSn_6-type), and RNi_4Sn_2 (KAu_4Sn_2-type), discussed in detail by Skolozdra in [1]. More recently, a series of isotypic R_2Ni_2Sn compounds with Mo_2NiB_2-type was found for *R* = Ce, Nd, Gd, Tb, and Dy and studied in [2]. Because of the potential for complex electrical and magnetic behavior arising from the coupling of *f*- and *d*-electrons in rare-earth – transition metal intermetallics, the properties of stannides are being investigated. Especially, the magnetic properties have been investigated in detail for most of these compounds [1,3-7]; the intermetallics with magnetic rare-earth elements generally order at low temperatures.

We recently studied electrical transport properties of the series RNi_3Sn_2 ternary stannides (*R* = Y, Sm, Gd, Tb, and Dy) with $HoGa_{2.4}Ni_{2.6}$-type structure. All of the investigated compounds exhibit metallic-like behavior; electronic structure calculations performed on YNi_3Sn_2 and $GdNi_3Sn_2$ confirmed metallic-like conductivity as reported in [8].

In this work we present electrical transport properties for *R*NiSn intermetallics (*R* = Y, Gd, Tb, Dy, and Lu) in the temperature range 80-380 K and the results of the electronic structure calculations. The experimental studies of the electrical resistivity and thermopower are accompanied by theoretical calculations of the density of states (DOS) for all the title compounds.

2. Experimental details

*R*NiSn (*R* = Y, Gd, Tb, Dy, and Lu) samples were prepared using an electric arc furnace by direct arc melting of the constituent elements (overall purity: *R* – 99.9 wt.%, Ni – 99.99 wt.%, and Sn – 99.999 wt.%) under a purified argon atmosphere. The alloys were subsequently annealed at 870 K for 720 hours and then cold water quenched. The phase composition and crystallographic parameters of the samples were determined from X-ray powder patterns recorded with a DRON-2.0m powder diffractometer (Fe K_α radiation). The determination of the crystallographic parameters was performed using the CSD program package [9].

The electrical resistivity was measured employing the two-probe method in the temperature range 80-380 K on millimeter-scale, well-shaped pieces cut by spark erosion from polycrystalline samples. Thermoelectric power measurements were carried out

Table 1 Lattice parameters and electrotransport characteristics for *R*NiSn compounds (*R* = Y, Gd, Tb, Dy, and Lu, TiNiSi-type).

Compound	Lattice parameters (nm)			$S_{300\ K}$ (μV/K)	$\rho_{380\ K}$ (μΩ m)
	a	*b*	*c*		
YNiSn	0.7113(2)	0.4446(1)	0.7661(3)	-3.6	1.06
GdNiSn	0.7236(3)	0.4461(1)	0.7676(4)	-7.6	1.43
TbNiSn	0.7143(2)	0.4445(3)	0.7663(5)	-5.8	0.58
DyNiSn	0.7096(4)	0.4439(2)	0.7657(8)	-6.0	2.17
LuNiSn	0.6935(5)	0.4393(9)	0.7602(2)	-7.2	0.96

using a standard differential method in the temperature range 80-380 K with pure copper as a reference material.

3. Electronic structure calculations

We used a FLAPW method [10] that performs DFT calculations using the local density approximation with wave functions as a basis. The Kohn-Sham equation and energy functional are evaluated consistently using the Full Potential Linearized Augmented Plane Wave (FLAPW) method. For this method, the space is divided into interstitial and non overlapping muffin tin spheres centered at the atomic sites. The employed basis function inside each atomic sphere is a linear expansion of the radial solution of a spherical potential multiplied by spherical harmonics. In the interstitial region, the wave function is taken as an expansion of plane waves and no shape approximation for the potential is introduced in this region, which is consistent with the full potential method. The core electrons are described by atomic wave functions, which are solved relativistically using the current spherical part; the valence electrons were also treated relativistically in our case. These FLAPW calculations were performed with the crystal structure parameters derived from our X-ray measurements. The spin polarized potential, spin orbit coupling, and the ferromagnetic state in these compounds were taken into account.

4. Results and discussion

The crystal structures of the *R*NiSn compounds (*R* = La-Lu) have been studied by different authors [11-13]. The compounds crystallize with the orthorhombic TiNiSi-type structure (space group *Pnma*), which is an ordered derivative of the $PbCl_2$-type. The results of magnetic properties measurements of these intermetallics were discussed in detail in [1,14]. YNiSn and LuNiSn are Pauli paramagnets, and the GdNiSn, TbNiSn and DyNiSn intermetallics are antiferromagnetically ordered at low temperatures.

The X-ray powder diffraction analysis revealed that the YNiSn, GdNiSn, TbNiSn, DyNiSn, and LuNiSn compounds synthesized in this work were single phases of TiNiSi-type crystal structure with trigonal prismatic coordination for the Ni-atoms (Fig. 1). Lattice parameters for all the investigated intermetallics are listed in Table 1.

The electrical resistivity (ρ) of the *R*NiSn intermetallics (*R* = Y, Gd, Tb, Dy, and Lu) is shown in Fig. 2. All the studied compounds show metallic behavior in the investigated temperature range. The electrical resistivity of increases with increasing temperature in the temperature range from 80 K to 380 K and is typical for intermetallics. The absolute values of the resistivity are small, of the order of 0.2-0.8 μΩ m at 80 K, and with increasing temperature the resistivity changes weakly to 0.61-2.25 μΩ m at 380 K (Table 1). It is worth noticing that the GdNiSn and DyNiSn stannides with magnetic rare earths are characterized by higher ρ values (0.75-2.17 μΩ m) compared to the non-magnetic YNiSn and LuNiSn compounds with maximal ρ values of the order of 1.09 and 0.83 μΩ m, respectively. In the case of the TbNiSn compound the values of the resistivity are smaller than for the stannides with Gd and Dy, which can be associated with microstructural features of the prepared sample. The electric transport properties of the LaNiSn and CeNiSn intermetallics have been investigated earlier [15,16], and it was shown that LaNiSn is characterized by metallic-like conductivity, whereas the $\rho(T)$ dependence for the CeNiSn stannide is typical for compounds with a Kondo lattice.

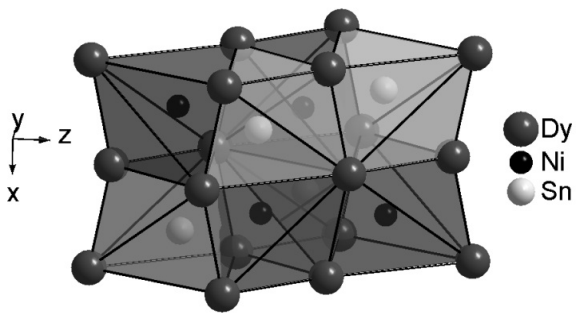

Fig. 1 Model of the DyNiSn structure with TiNiSi-type.

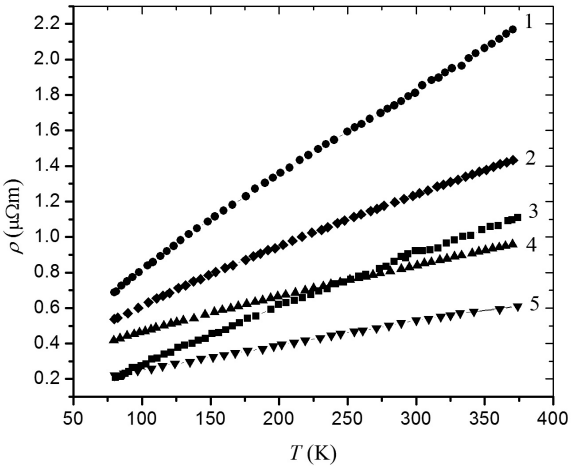

Fig. 2 Temperature dependence of the electrical resistivity for DyNiSn (1), GdNiSn (2), YNiSn (3); LuNiSn (4), and TbNiSn (5).

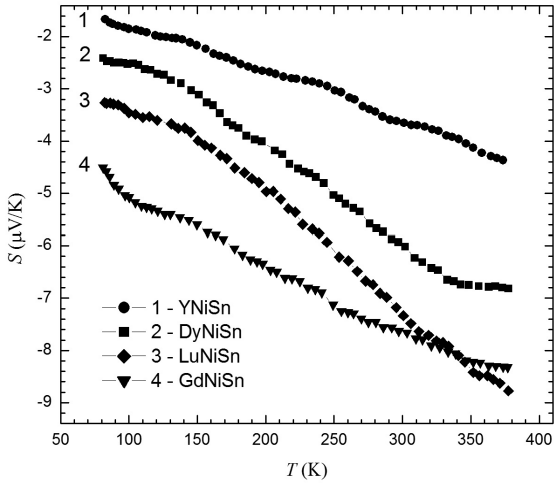

Fig. 3 Temperature dependence of the thermopower for YNiSn (1), DyNiSn (2), LuNiSn (3), and GdNiSn (4).

The temperature dependencies of the Seebeck coefficient $S(T)$ for the *R*NiSn compounds are shown in Fig. 3. The thermoelectric power of all the studied compounds shows very similar temperature dependence, decreasing with increasing temperature, and exhibits small negative values at 300 K (see Table 1), with the smallest S for YNiSn (-3.6 μV/K) and values of the order of about (-6) - (-7) μV/K for the rest of the compounds. For the previously studied LaNiSn intermetallic, the S value is typically -10.0 μV/K at 300 K, whereas the CeNiSn compound is characterized by a positive value of the Seebeck coefficient (8.1 μV/K).

Analysis of the electrical transport properties from measurements performed on different series of *R*-Ni-Sn compounds, *e.g.* RNi_3Sn_2, $R_9Ni_{24}Sn_{49}$, $RNiSn_4$, *R*NiSn, and $RNiSn_2$ (for light lanthanides) showed a similar metallic conductivity with small values of the electrical resistivity.

Electronic structure calculations applying the FLAPW method were performed using the space group and the cell parameters obtained from X-ray diffraction refinements for YNiSn, GdNiSn and LuNiSn. The calculated densities of states (DOS) are presented in Figs. 4, 5 and 6. The non-zero DOS at the Fermi level confirms the metallic character of these compounds. The Fermi level, taken as a reference, is located in a DOS valley, which explains the structural stability of the materials. The DOS also indicates that the contributions of the Ni and Sn atoms to the total DOS are similar and that the shape changes are induced by the 5*d* electrons of the Gd and Lu atoms.

The valence band for YNiSn essentially originates from Ni contributions with *d*-band character since the Ni valence band is mainly from the *d*-band (Fig. 4). The unoccupied states show contributions arising from the Y *d*-band, while at lower energies (~7 eV) the DOS exhibits contributions from the Sn atoms with *s* and *p* character.

For GdNiSn, the DOS, shown in Fig. 5, is dominated by Gd *f*-band, which contributes to both the occupied and unoccupied states since this band, which is half full, is magnetically polarized. The other contributions, which are from Ni and Sn, are similar to those found in the DOS of YNiSn. For the DOS of LuNiSn (see Fig. 6), the additional peaks located in the valence band at ~-5 eV are assigned to the Lu *f*-band. The peaks in the major spin DOS and the minor spin DOS are symmetric with respect to the energy axis since the *f*-band of the Lu atoms, completely full, is magnetically unpolarized. The calculations, done with the spin polarized potential in the ferromagnetic model, reveal a marked polarization of the effective Gd *f*-band that induces a magnetic moment on the Gd atom equal to 6.87 μ_B, which we consider in fair agreement with the pure metal moment (~7 μ_B). The charge of the interstitial zone in the cell was also found to be polarized with a magnetic moment of 0.76 μ_B.

5. Conclusion

Measurements of the resistivity for all the studied *R*NiSn stannides show a metallic-like behavior of the conductivity in the investigated temperature range. The electrical resistivity linearly increases with increasing temperature. Measurements of the Seebeck coefficient revealed that the thermoelectric power decrease with increasing temperature, exhibiting very similar temperature dependence.

Electronic structure calculations confirmed the metallic character of the compounds and evidenced that the Ni and Sn contributions to the DOS are similar in YNiSn, GdNiSn and LuNiSn. The changes of the DOS shape are due to the different rare earth ions.

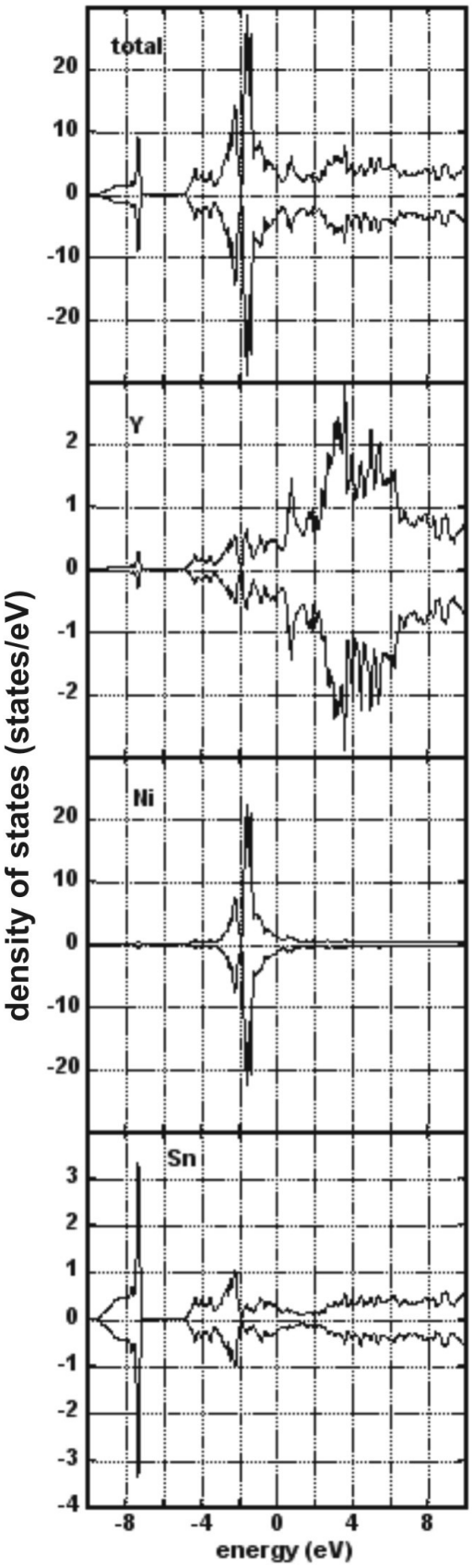

Fig. 4 DOS of the majority spin and the minority spin in YNiSn from FLAPW calculations.

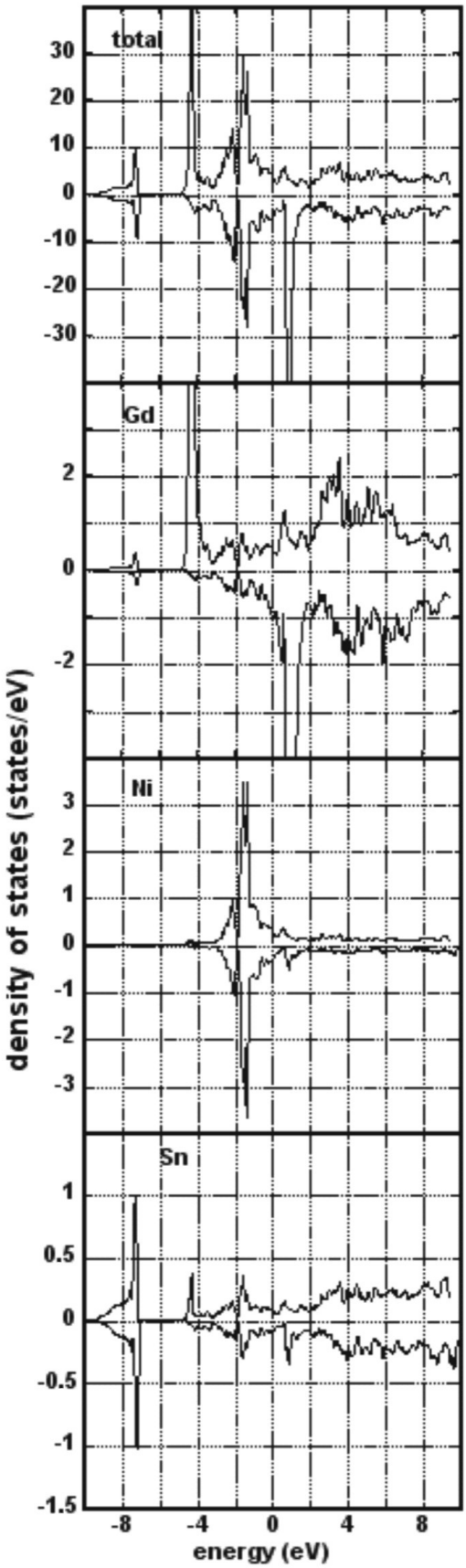

Fig. 5 DOS of the majority spin and the minority spin in GdNiSn from FLAPW calculations.

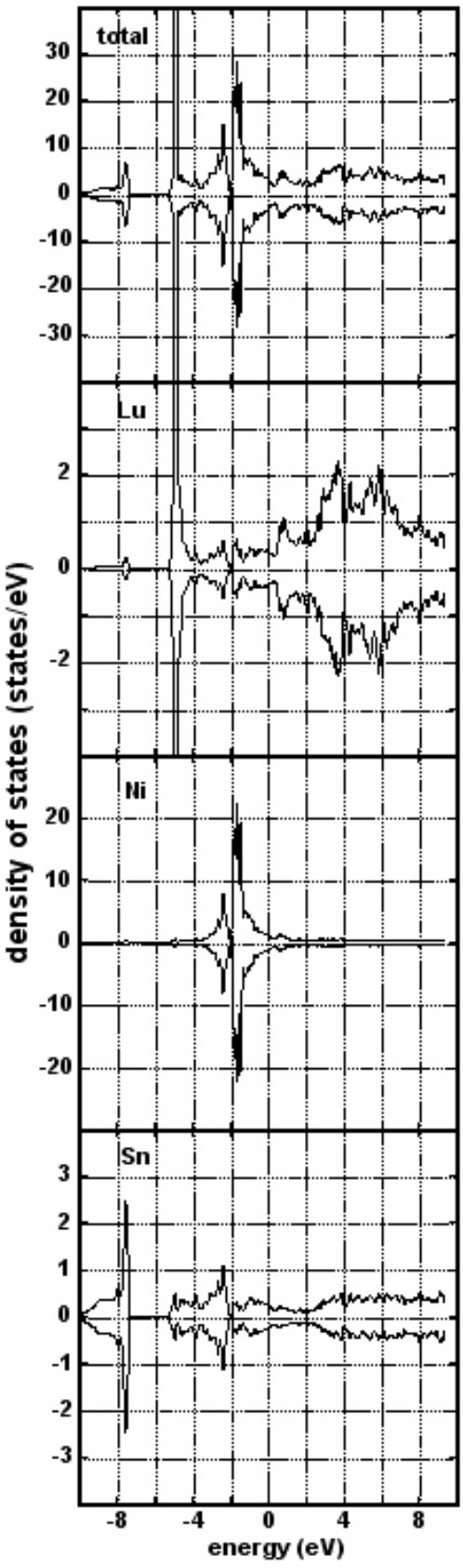

Fig. 6 DOS of the majority spin and the minority spin in LuNiSn from FLAPW calculations.

The electronic structure calculations showed, as expected, a marked polarization of the *f*-band for Gd in GdNiSn, in fair agreement with the pure metal behavior.

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