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MAGNETIC AND TRANSPORT PROPERTIES OF RNiSb COMPOUNDS (R = Gd, Tb, Dy, Yb, Lu)

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The structural, magnetic, electrical and thermoelectric properties of heavy rare-earths ternary compounds RNiSb were investigated. Except Yb-based compound (and nonmagnetic Lu), all compounds are low temperature antiferromagnets. $YbNi_{0.9}Sb$ reflects some mixed valence behaviour. Magnitude of the resistivity indicates that investigated compounds are semimetals or high doped semiconductors.

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1. Introduction

Rare earths form with antimony the RSb compounds with the crystal structure of the NaCl type [1]. The structure of NaCl contains 8 tetrahedral vacancies in the unit cell (or else two vacancies on the formula). The crystal structure of RNiSb (R = heavy earths) belongs to the MgAgAs type (space group $F43m$) and is a derivative of the RSb structure. It can be made by a regular insertion of 4 nickel atoms in the tetrahedral vacancies (e.g. lattice parameter for TbSb is equal to 6.17 Å, whereas for TbNiSb — 6.33 Å). Light rare earths form RNiSb compounds with the hexagonal AlB_2 type [1, 2]. GdNiSb occurs in two crystal modifications: high temperature (HT) one of AlB_2 type and the low temperature (LT) of MgAgAs type [1, 2].

The study of the magnetic, transport and structural properties of RNiSb, where R = Gd, Tb, Dy, Yb, Lu became the subject of the present paper.

2. Results

GdNiSb. The low-temperature modification LT-GdNiSb shows antiferromagnetic transition at $T_N = 3.7$ K, whereas the high-temperature modification HT-GdNiSb undergoes a sort of antiferromagnetic phase transition with $T_N = 3.3$ K. The resistivities of both samples are different by their magnitudes (Fig. 1a, b). Distinct kinks on the $\rho(T)$ curves of both modifications appear in the region of

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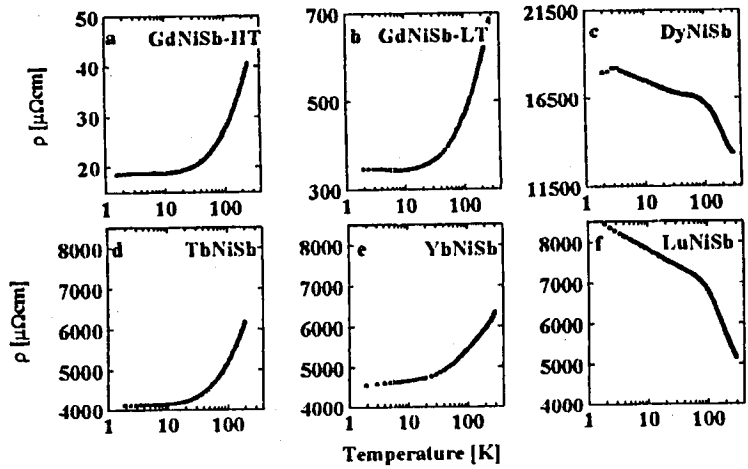

Fig. 1. Resistivity of the RNiSb compounds.

the low temperature magnetic transitions. The magnetoresistance was measured on LT-GdNiSb (applied field 0–4 T). It is negative and reaches 8.7% at 2 K under 4 T. The thermopower — S of LT-GdNiSb is positive and increases linearly with the temperature. The largest value of S is $S = 58$ μV/K at 380 K. The thermopower of HT-GdNiSb is smaller than that of LT-GdNiSb, its maximum value is equal to 10 μV/K at 380 K.

DyNiSb. The thermal dependence of the reciprocal susceptibility is linear down to 4 K, no deviation from the Curie–Weiss law is observed. The resistivity is characterized by a large magnitude (Fig. 1c). The resistivity falls below 3 K indicating a magnetic transition between 2 and 3 K (the magnetic properties of DyNiSb were measured only down to 4 K). The $S(T)$ dependence is linear and its value at 380 K is equal to 98 μV/K. An applied magnetic field strongly reduces the resistivity of DyNiSb. The maximum of resistivity at 0.5 T indicates that the magnetic structure is complex.

TbNiSb. The compound undergoes an antiferromagnetic phase transition at 5 K which is well observed on the $\chi(T)$ curve. The $M(H)$ dependence is almost linear at 2, 6 and 12 K. The resistivity of this sample has a kink at 6 K, which confirms an antiferromagnetic ordering (Fig. 1d). The magnetoresistance is negative and reaches 2.7% at 2 K. The thermopower is very small, its maximum value is 5.2 μV/K at 380 K.

$YbNi_{0.9}Sb$. The exact structure analysis showed that in this compound the deficiency of Ni in amount of 0.1 per formula is present. The reciprocal susceptibility deviates from the linearity below 10 K and tends to flatten. The magnetization curves $M(H)$ are very well described by Langevin function down to 1.5 K (Fig. 2a). The lowering of high temperature μ_{eff} indicates for intermediate valence state (IVS). The analysis of μ_{eff} (Fig. 2b) shows that spin fluctuation temperature is about 15 K. The IVS can be confirmed by some increase in the lattice

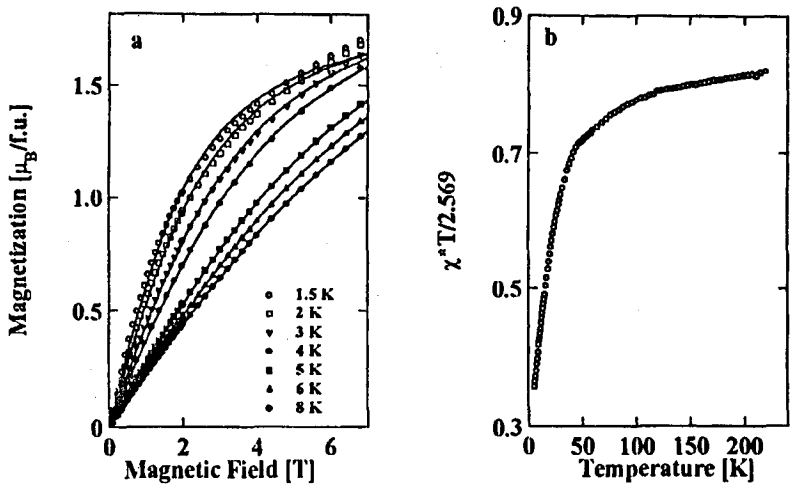

Fig. 2. (a) Magnetic isotherms for $YbNi_{0.9}Sb$. The solid lines represent a fit to the Langevin function. (b) Magnetic effective moment of $YbNi_{0.9}Sb$ vs. temperature.

parameter of $YbNi_{0.9}Sb$ in comparison with that of TmNiSb ($a = 6.225$ Å [2]), in spite of the deficiency in Ni content. The thermopower is not large (26 μV/K at 380 K).

LuNiSb. The properties of LuNiSb were measured in the region between 80–380 K. LuNiSb is a Pauli paramagnet, its value $\chi = 3.55 \times 10^{-6}$ emu/mole at room temperature. The resistivity decreases with temperature (Fig. 1f). The $S(T)$ dependence is linear (50 μV/K and 136 μV/K at 100 K and 380 K respectively).

TABLE

Structural and magnetic properties of RNiSb compounds.

Compound	a [Å]	θ_p [K]	μ_{eff} [μ_B]	T_N [K]
HT-GdNiSb (AlB_2)	$a = 4.373$ $c = 3.743$	−29	8.6	3.3
LT-GdNiSb (MgAgAs)	6.338	−13	8.9	3.7
TbNiSb	6.330	−25	10.7	5.1
DyNiSb	6.303	−15.5	10.97	2–3*
YbNiSb	6.238	−8.5	4.09	15**
LuNiSb	6.210	Pauli paramagnet		

*According to resistivity.

**Spin fluctuation temperature.

3. Discussion

The investigated compounds with the MgAgAs structure type are characterized by rather large magnitudes of the resistivity and thermopower whose values exceed considerably those of metals and intermetallics. The thermal dependence of these properties and their dependence on sample preparation indicate that the RNiSb compounds are strongly doped semiconductors or semimetals. The semiconductor properties of RNiSb can be explained by the peculiarity of their crystal structure and electronic concentration of 8 electron/f.u. (valence of R, Ni and Sb is equal to 3, 0, 5 respectively). The coordination of R and Sb atoms is tetrahedral, which favours the formation of covalent chemical bonds. The change of the crystal structure or electronic concentration leads to a break of the covalent bonds and the compound becomes metallic. Therefore the HT-GdNiSb (AlB_2 structure type), which has another structure with a trigonal prismatic coordination, shows metallic properties. Similar change of properties also occurs between ZrNiSn compound (MgAgAs type, semiconductor) and ZrCoSn (Fe_2P type, metal) [3]. Apparently the more metallic properties of $YbNi_{0.9}Sb$ than in the other compounds with MgAgAs type structure can be explained by a deviation of its composition from the stoichiometric one.

The RNiSb compounds have lower Néel points than those of the RSb compounds, which form complex noncollinear magnetic structures. An inclusion of the Ni atoms in the RSb structure reduces the exchange interactions between the R atoms. From the shape of the magnetization and magnetoresistivity curves, the magnetic structures of RNiSb are also possibly complex and noncollinear. It seems that the complicated magnetic and transport properties of RNiSb compounds may be related, as those of the RSb compounds [4], to the competition between several effects such as the crystalline electric field effects, magnetic exchange interactions, Kondo effect (for YbNiSb) and also to the trend to form a dielectric gap.

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