Structural, magnetic and electronic transport studies of RAgSn_2 compounds ($\text{R} = \text{Y, Tb, Dy, Ho}$ and Er) with Cu_3Au -type

L ROMAKA^a, V V ROMAKA^b, I LOTOTSKA^a, A SZYTULA^c, B KUZHEL^a, A ZARZYCKI^c,
E K HLIL^{d,*} and D FRUCHAR^d

^aDepartment of Inorganic Chemistry, Ivan Franko Lviv National University, Kyryl and Mephodi Street 6, 79005, Lviv, Ukraine

^bDepartment of Materials Engineering and Applied Physics, Lviv Polytechnic National University, Ustyianovycha Street 5, 79013, Lviv, Ukraine

^cInstitute of Physics, Jagiellonian University, Reymonta 4, 30059 Krakow, Poland

^dInstitut Néel, CNRS et Université Joseph Fourier, BP 166, F-38042 Grenoble cedex 9, France

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Abstract. RAgSn_2 compounds, where $\text{R} = \text{Y, Tb, Dy, Ho}$ and Er , were synthesized by arc-melting and subsequent annealing at 870 K. The formation of cubic phases with Cu_3Au -type structure (space group $Pm\bar{3}m$) was studied. Magnetic property measurements showed that in paramagnetic state, the compounds with magnetic rare-earth atoms are Curie–Weiss paramagnets and order antiferromagnetically at low temperatures. YAgSn_2 is a Pauli paramagnet in 100–300 K temperature range. The electrical properties of RAgSn_2 compounds were investigated by means of electrical resistivity and Seebeck coefficient measurements in 4.2–300 K temperature range. All investigated compounds exhibit metallic type of conductivity. Electronic structure calculations based on full potential linearized augmented plane wave (FLAPW) method is also carried out to probe the magnetic and electronic structures of RAgSn_2 compounds. Comparisons between experimental data and calculations are discussed.

Keywords. Intermetallics; crystal structure; magnetic properties; electric properties; electronic structure calculations.

1. Introduction

The ternary phases with cubic Cu_3Au -type were previously reported in $\{\text{Ti, Zr, Hf}\}\text{-Ag-X}$ ($\text{X}=\text{Al, Ga, In}$) systems (Mabuchi and Nakayama 1991; Gulay and Zaremba 1999; Kotur and Verbovitskii 2000; Verbovitskii and Kotur 2003). These phases are characterized by significant homogeneity range along the isoconcentrate of 25 at% Me (Ti, Zr or Hf) leading to the composition MeX_3 . In Kotur and Verbovitskii (2000) and Verbovitskii and Latka (2007), the authors explain the formation of these cubic ternary phases in $\{\text{Ti, Zr}\}\text{-Ag-}\{\text{Al, Ga}\}$ systems by morphotropic transformation of the corresponding binary phases TiAl_3 (TiAl_3 -type) and ZrAl_3 (ZrAl_3 -type) due to substitution of Al (or Ga) atoms by Ag in the ternary region, which stabilizes the metastable MeX_3 compounds with Cu_3Au -type (Colinet and Pasturel 2001). Later, the ternary compounds with Cu_3Au -type were also found with rare-earth elements, silver and lead (Gulay and Wolcyrz 2001) and in R-Ag-Sn systems, where R is heavy rare-earths (Romaka *et al* 2007a, 2008a; Liang *et al* 2010b).

A review of the literature data showed that in R-Ag-Sn systems with heavy rare-earths, two series of intermediate

ternary phases were previously known to exist, i.e. RAgSn and $\text{R}_3\text{Ag}_4\text{Sn}_4$ compounds (Mazzone *et al* 1981; Pöttgen 1996; Katon *et al* 1997; Romaka *et al* 2007b). $\text{R}_3\text{Ag}_4\text{Sn}_4$ compounds are characterized by orthorhombic $\text{Gd}_3\text{Ag}_4\text{Ge}_4$ -type structure (Romaka *et al* 2007b), while RAgSn stannides crystallize in different structural types depending on the size and valence state of rare-earth elements— LiGaGe -type for Y, Gd–Er, CaLiSn -type for Yb, both derivatives of AlB_2 -type (Mazzone *et al* 1981; Katon *et al* 1997), CeCu_2 -type for EuAgSn (Pöttgen 1996), and TmAgSn and LuAgSn compounds belong to the hexagonal ZrNiAl -type (Sebastian *et al* 2006). Additionally, structural transition from LiGaGe -type to the high pressure modification with ZrNiAl -type was observed for ErAgSn compound (Matar *et al* 2012). Numerous magnetic property investigations of RAgSn intermetallics with magnetic rare-earths display that antiferromagnetic interaction is predominant in these compounds at low temperatures (Adam *et al* 1990; Bazela *et al* 1995; Baran *et al* 1997), TmAgSn is Curie–Weiss paramagnet down to 2 K, while YAgSn and LuAgSn intermetallics showed Pauli paramagnetism (Sebastian *et al* 2006). As reported in Pöttgen *et al* (1999), YbAgSn stannide is characterized by Pauli paramagnetism caused by divalent state of Yb atoms and metallic type of conductivity. Magnetic property measurements performed on $\text{Gd}_3\text{Ag}_4\text{Sn}_4$ and $\text{Sm}_3\text{Ag}_4\text{Sn}_4$ stannides indicated antiferromagnetic ordering at $T_N = 8$ K and $T_N = 9$ K,

* Author for correspondence (hlil@grenoble.cnrs.fr)

respectively (Mazzone *et al* 2005). Later, the antiferromagnetic ordering at low temperatures was observed for other isotypic compounds, $\text{Pr}_3\text{Ag}_4\text{Sn}_4$ and $\text{Nd}_3\text{Ag}_4\text{Sn}_4$ (Penc *et al* 2007).

In this paper, the study of magnetic and electrical characteristics of RAgSn_2 compounds, where $\text{R} = \text{Y, Tb, Dy, Ho}$ and Er , is carried out. In addition, electronic structure calculations are reported and discussed.

2. Experimental

Polycrystalline samples of $\text{R}_{25}\text{Ag}_{25}\text{Sn}_{50}$ composition with $\text{R} = \text{Y, Tb, Dy, Ho}$ and Er were prepared by arc melting the stoichiometric amounts of the constituent elements (nominal purities: rare-earths –99.9, Ag –99.99, Sn –99.999 wt%) on a water-cooled copper hearth under a protective Ti-gettered argon atmosphere. Subsequently, the obtained samples were annealed at 870 K for 720 h in an evacuated silica tubes, followed by quenching in cold water. The phase purity and final sample composition were controlled by electron probe micro-analysis (EPMA) on Carl Zeiss DSM 962 equipped with Link EDX system operating at 20 kV and 60 mA.

The phase analysis and the estimate of crystallographic parameters were performed using X-ray powder patterns recorded with HZ-4A and Bruker D8 powder diffractometers, both at $\text{CuK}\alpha$ radiation. Determination of crystallographic parameters were performed using the WinPLOT program packages (Roisnel and Rodriguez-Carvajal 2001).

Magnetic measurements were performed in 2–300 K temperature range under applied magnetic fields up to 50 KOe using Quantum Design MPMS-5 SQUID magnetometer. The electrical resistivity was measured in 4.2–300 K temperature range employing two-probe method on the millimeter-scale, well-shaped pieces cut by spark erosion from the polycrystalline samples. The thermoelectric power measurements were carried out using a standard differential method with pure copper as a reference material in 4.2–300 K temperature range.

3. Details of structure electronic calculation

We used FLAPW method (Blaha *et al* 1990) which performs DFT calculations using the local density approximation with wavefunctions as a basis. Kohn–Sham equation and energy functional are evaluated consistently using full potential linearized augmented plane wave (FLAPW) method. For this method, the space is divided into interstitial and non-overlapping muffin tin spheres centred on the atomic site. 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 wavefunction 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 wavefunctions which

are solved relativistically using the current spherical part; the valence electrons are also treated relativistically in our case. These FLAPW calculations are performed with the crystal structure parameters obtained from our X-ray measurements. Spin–orbit coupling is taken into account for $\text{R} = \text{Tb–Er}$ as well.

4. Results and discussion

4.1 Formation of ternary phases with Cu_3Au -type in R–Ag–Sn systems

Among the studied R–Me–Sn ternary systems (Me–3d -element), formation of the ternary cubic compounds RAgSn_2 with Cu_3Au -type was observed only in rare-earth silver–tin systems ($\text{R} = \text{Y, Tb, Dy, Ho}$ and Er). Analysis of the literature data showed that formation of the ternary cubic phases with Cu_3Au -type in R–Ag–Sn systems is directly related to the binary RSn_3 compounds. RSn_3 binaries with light rare-earths (La–Sm) crystallize in cubic Cu_3Au -type (Borzone *et al* 1983; Kletowski 1987; Canepa *et al* 1989; Weitzer *et al* 1992), whereas, RSn_3 compounds where R are heavy rare-earths belong to the orthorhombic $\text{GdSn}_{2.75}$ -type (space group $\text{Amm}2$) (Skolozdra *et al* 1986; Koretskaya *et al* 1988; Palenzona and Manfrinetti 1993). According to Miller and Hall (1972), the cubic modification of Cu_3Au -type for RSn_3 compounds, where $\text{R} = \text{Y, Tb, Dy, Ho}$, and Er was found at high pressure.

Taking into account these data confirmed by numerous investigations of the corresponding ternary systems, R–Me–Sn , we can assert that in case of cerium group elements where the binary compounds, RSn_3 , crystallize with cubic Cu_3Au -type, the ternary intermediate phases in R–Ag–Sn systems with analogous structure were not observed. This fact was successfully confirmed during the study of $\{\text{La, Ce, Pr, Nd}\}\text{–Ag–Sn}$ phase diagrams (Salamakha *et al* 1996; Boulet *et al* 1999; Mazzone *et al* 2002; Liang *et al* 2010a). In R–Ag–Sn systems where $\text{R} = \text{Y, Tb, Dy, Ho}$ and Er , in the ternary region, the substitution of Sn atoms by Ag along the isoconcentrate of 25 at% R , including the stoichiometry 1:1:2, results in the formation of cubic ternary RAgSn_2 phases. These phases have the same structure as the high pressure RSn_3 binaries (Cu_3Au -type, space group $\text{Pm}\bar{3}m$) with distribution of R atoms at crystallographic position 1a (0 0 0) and statistical mixture (Ag, Sn) - at 3c (0 1/2 1/2). Thus, chemical formula of the compounds should be written as RAgSn_2 and it is in good agreement with EPMA data ($\text{R}_{25.58–25.64}\text{Ag}_{23.33–23.70}\text{Sn}_{52.04–52.7}$). We can assert that partial replacement of Sn atoms by Ag ($r_a(\text{Ag}) = 0.145 \text{ nm}$) leads to the homeotypic transformation of structure: $\text{GdSn}_{2.75}$ -type $\rightarrow \text{Cu}_3\text{Au}$ -type, i.e. stabilization of Cu_3Au cubic modification in the ternary region. Analysing both crystal structures, we have noticed that orthorhombic $\text{GdSn}_{2.75}$ structure consists of the fragment of cubic Cu_3Au -type. For example, the structural relationship between binary $\text{DySn}_{2.75}$ (orthorhombic $\text{GdSn}_{2.75}$ -type)

Figure 1. Structural relationship between DySn_{2.75} (GdSn_{2.75}-type) and DyAgSn₂ (Cu₃Au-type) structures.

Figure 2. Temperature dependence of reciprocal magnetic susceptibility of DyAgSn₂ and ErAgSn₂. Inset presents the low-temperature dependence of magnetic susceptibility.

and ternary DyAgSn₂ (cubic Cu₃Au-type) compounds are shown in figure 1. Otherwise, in Gd case (presence of two polymorphic modifications of GdSn₃ binary (Palenzona and Manfrinetti 1993)), substitution of Sn atoms by Ag along with the isoconcentrate of 25 at% Gd occurs strongly depending on the temperature and should be studied more accurately.

4.2 Magnetic and transport properties

Two types of measurements were performed on RAgSn₂ samples: magnetic susceptibility measurements under a magnetic field of up to 1 kOe in the 2–300 K temperature range (from these data, the effective magnetic moment μ_{eff} and the paramagnetic Curie temperature θ_p were obtained) and magnetization measurements under magnetic fields of up to 50 kOe and $T = 2$ K (in order to get the value of pseudo-saturated magnetic moment and the character of magnetization curve). Figures 2 and 3 show temperature dependence of the reciprocal magnetic susceptibilities in 2–300 K temperature range. In this region, the temperature $\chi'(T)$ dependence for RAgSn₂ (R = Tb, Dy, Ho and Er) obey Curie–Weiss law

Figure 3. Temperature dependence of reciprocal magnetic susceptibility of HoAgSn₂ and TbAgSn₂. Inset presents the low-temperature dependence of magnetic susceptibility.

with negative values of the paramagnetic Curie temperature and the effective magnetic moment μ_{eff} near to the free R³⁺ ion values (see table 1). The low temperature magnetic susceptibility of RAgSn₂ compounds, where R = Tb, Dy, Ho and Er measured under a field of 1 kOe are reported in the insets of figures 2 and 3. A pronounced maximum characteristic of an antiferromagnetic ordering is observed for all studied compounds at corresponding T_N (table 1). This agrees fairly with the thermal dependence of electrical resistivity (see table 1).

For TbAgSn₂ stannide, a maximum is much more spread out than for the other compounds. Looking carefully, it a slight anomaly at 20 K can be observed whereas the maximum occurs at 14 K. In fact, this behaviour is quite similar to that observed in TbRu₂Ge₂ compound, where it has been extensively studied by magnetization and neutron diffraction experiments on both polycrystalline samples and single crystal (Garnier *et al* 1995) and a transition from one antiferromagnetic structure to another is reported. For both structures, slightly different magnetic periodicities were detected. Later, a similar behaviour was observed for TbNi₃Sn₂ stannide (Romaka *et al* 2008b). So, we can conclude that a similar behaviour likely occurs in TbAgSn₂.

Temperature dependence of the magnetic susceptibility for YAgSn₂ stannide was measured by Faraday method in 100–300 K temperature range and under a magnetic field of up to 0.8 T (figure 4). The susceptibility values remain in the order of 10^{−5} emu/mol in the investigated temperature range which indicated Pauli paramagnetism for Y compound. The slight increase observed at low temperature could arise from impurity having a localized paramagnetic behaviour.

The magnetization curves at 2 K are nearly linear functions of the external magnetic field up to 50 kOe (see figure 5), no saturation of $M(H)$ is observed up to 50 kOe. The field

variation of the magnetization for all studied compounds is taken at 2 K being characteristic of the paramagnets.

We have mentioned above that RAgSn_2 compounds crystallize in cubic Cu_3Au -type structure, where R atoms are distributed in crystallographic position $1a$ (0 0 0) and (Ag, Sn) - in $3c$ (0 1/2 1/2). Thus, in these compounds large R-R interatomic distances (in the order of 0.45 nm) exclude any direct magnetic interactions. The magnetic ordering observed at low temperatures for $\text{R} = \text{Tb-Er}$ is due to the long range magnetic interactions transferred via the conduction band electrons, which is the mechanism described by RKKY model. In this case, the paramagnetic Curie θ_p and Neel T_N temperatures should be proportional to de Gennes factor, $G = (g-1)^2 J(J+1)$, which is shown in figure 6 for the studied phases.

Results of electrical resistivity and thermoelectric power measurements performed on RAgSn_2 intermetallics ($\text{R} = \text{Y, Tb-Er}$) are displayed in figure 7. All investigated compounds show metallic-like behaviour of conductivity in the investigated temperature range. Their resistivity at room temperature is of the order of 0.72–1.43 $\mu\Omega\cdot\text{m}$ and with decreasing

temperature, it continuously decreases up to 4.2 K with absolute values of about 0.42–1.03 $\mu\Omega\cdot\text{m}$. For magnetically ordered compounds ($\text{R} = \text{Tb, Dy, Ho}$ and Er), more or less change of slope on $\rho(T)$ dependencies is observed at transition temperature (T_{tr}) close to T_N . In the ordered state, the resistivity for these compounds decreases more rapidly due to gradual suppression in scattering conduction electrons on disordered magnetic moments.

The thermoelectric power of all studied compounds shows very similar temperature dependencies (see figure 8, a and b). At 5 K, it is slightly positive (0.02–0.09 $\mu\text{V/K}$ for $\text{R} = \text{Y, Tb, Ho, Er}$ and 1.1 $\mu\text{V/K}$ for Dy) and decreases with increasing temperature up to 300 K (–1.03–2.1 $\mu\text{V/K}$), thus, indicating the dominance of electronic-type conductivity. The total change in Seebeck coefficient is very small (~ 2 $\mu\text{V/K}$), consistent with metallic character of all the investigated stanides. The behaviours of thermopower vs temperature are similar for all studied RAgSn_2 compounds, including magnetic rare-earths (Tb–Er) and non-magnetic Y. The insignificant anomalous $S(T)$ at about 50 K may be caused by the very small values of absolute thermopower in this range and

Table 1. Lattice parameters and magnetic data for RAgSn_2 compounds from magnetic and electric resistivity measurements.

R	a , nm	$T_N(\text{K})$		$\theta_p(\text{K})$	$\mu_{\text{eff}}(\mu_B)$	
		M^*	R^{**}		Exp.	Theor.
Tb	0.45504(3)	14.0	12.5	–43.1(1)	9.66(1)	9.72
Dy	0.45308(1)	9.5	9.8	–26.3(1)	10.53(1)	10.65
Ho	0.45198(2)	6.5	9	–14.8(1)	10.42(1)	10.61
Er	0.45143(2)	4.9	8.8	–8.6(1)	9.45(1)	9.58
Y	0.45634(2)			Pauli paramagnet		

M^* - from the magnetic data.

R^{**} - from the electrical resistivity measurements.

Figure 4. Temperature dependence of magnetic susceptibility of YAgSn_2 .

Figure 5. Low temperature thermal variation of magnetization vs applied field at 2 K for RAgSn_2 compounds.

Figure 6. Néel and paramagnetic Curie temperatures for RAgSn_2 compounds plotted as a function of de Gennes parameter.

Figure 7. Temperature dependencies of electrical resistivity of RAgSn_2 compounds.

also by the presence of a statistical distribution of (Ag, Sn) atoms in the crystal structure.

4.3 Electronic structure calculations

Total density of states (DOS) deduced from band structure calculations for all compounds (including Gd compound for comparison) are presented in figure 9. The main evidence is the absence of gap close to the Fermi level E_F (taken as energy reference) which confirms the conductor character of these alloys. Analysis details of total DOS points to the occupied states that are mainly originating from 4-*d* Ag in YAgSn_2 compound (see peak between -5.3 and -4.5 eV). In addition, the difference in DOS shape for spin-up and spin-down confirms the magnetic state for RAgSn_2 with magnetic

Figure 8. Temperature dependencies of thermoelectric power for RAgSn_2 compounds.

rare-earths ($\text{R} = \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}$ and Er). Except YAgSn_2 and GdAgSn_2 , for all remaining compounds ($\text{R} = \text{Tb}, \text{Dy}, \text{Ho}$ and Er), calculations were done with spin-orbit coupling effect. Here, it is worth to note that calculations are performed in the framework of antiferromagnetic state for RAgSn_2 ($\text{R} = \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}$ and Er) compounds. DOS shape change vs rare-earth metal type in these compounds are dominated by 4-*f* band contribution change. For further analysis, we report 4-*f* band in all these systems in figure 10. As expected, the fully 4-*f* spin-up and empty 4-*f* spin-down of Gd atom in GdAgSn_2 contribute to both occupied states (at -4.5 eV) and unoccupied states (at 0.5 eV). This splitting is induced by high exchange spin in Gd 4-*f* band since, $S = 7$.

For RAgSn_2 ($\text{R} = \text{Tb}, \text{Dy}, \text{Ho}$ and Er), the partially empty 4-*f* spin down band is located at Fermi level, while their fully spin-up band at -4 eV shift to Fermi level when Tb is replaced by Dy, Ho and Er, successively. This shift could be explained in terms of reduction of spin interaction exchange when S changes from $S = 7$ in Gd to $S = 2$ in Er.

Figure 9. Total DOS in RAgSn₂ compounds from FLAPW calculations.

Figure 10. 4*f* band contributions in RAgSn₂ compounds from FLAPW calculations.

Both rear-earth 4-*f* contributions in occupied states and at Fermi level shows splitting peaks (2 peaks for Tb, more than 2 peaks for Dy, Ho and Er). This inter-band splitting increases upon successive Re atoms ($R = \text{Tb, Dy, Ho and}$

Er). Such splitting increase could be reasonably explained in terms of increase of crystal field effect on asymmetric charge distribution related to 4*f* band with $L > 0$. Calculations allow for computing the localized magnetic moment on atoms as well. As example, we found 7.41 and 10.22 μ_B values for Gd and Dy in GdAgSn₂ and DyAgSn₂, respectively. Both values agree nicely with those obtained from magnetic measurements.

5. Conclusions

RAgSn₂ ($R = \text{Y, Tb, Dy, Ho and Er}$) compounds were investigated by magnetic and electrical measurements. All measurements point out to pertinent results such as their antiferromagnetic ordering at low temperature. The compounds have the metallic character of the electrical conductivity and characterize by the large R–R interatomic distances. A good agreement between experimental values of μ_{eff} and the corresponding values for R^{3+} ions confirmed RAgSn₂ formula of the investigated compounds.

Electronic structure calculations are also performed. They confirm the conductor character and the magnetic state of

RAgSn₂ compounds with R = Tb–Er. In addition, computed magnetic moment on rare-earth atoms agree nicely with experimental data.

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