Magnetic and electrical properties of the stannides $RE_3Co_6Sn_5$ (RE = Sm, Gd, Tb and Dy)

2003 J. Phys.: Condens. Matter 15 2515

(http://iopscience.iop.org/0953-8984/15/17/307)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **15** (2003) 2515–2522 PII: S0953-8984(03)59383-3

Magnetic and electrical properties of the stannides $RE_3Co_6Sn_5$ (RE = Sm, Gd, Tb and Dy)

D Kaczorowski[1,4], Ya Mudryk[2,3], P Rogl[2], L Romaka[3] and Yu Gorelenko[3]

[1] Institute of Low Temperature and Structure Research, Polish Academy of Sciences, PO Box 1410, 50-950 Wrocław 2, Poland
[2] Institut für Physikalische Chemie, Universität Wien, Währingerstraße 42, A-1090 Wien, Austria
[3] Lviv National University, Kyryla and Mefodia Street 6, 290005 Lviv, Ukraine

E-mail: dkaczor@int.pan.wroc.pl

Received 10 February 2003
Published 22 April 2003
Online at stacks.iop.org/JPhysCM/15/2515

Abstract

Polycrystalline samples of the ternary intermetallics $RE_3Co_6Sn_5$ (RE = Sm, Gd, Tb and Dy) were studied by means of magnetization, dc magnetic susceptibility and electrical resistivity measurements. All these stannides were found to order magnetically at low temperatures. $Sm_3Co_6Sn_5$ is antiferromagnetic below $T_N = 8$ K, while $Tb_3Co_6Sn_5$ exhibits ferromagnetic ordering below $T_C = 16$ K. The other two compounds show more complex magnetic behaviour with subsequent phase transitions in the ordered regions. For $Gd_3Co_6Sn_5$ one observes the onset of ferromagnetism at $T_C = 25$ K, which is followed by a change in the magnetic structure at $T_1 = 12$ K. In the case of $Dy_3Co_6Sn_5$ an antiferromagnetic type of order sets in at $T_N = 7$ K, and then a spin structure rearrangement occurs at $T_1 = 3$ K that yields a ferromagnetic component at lower temperatures. All the ternaries studied exhibit metallic-like conductivity with pronounced anomalies at the magnetic phase transitions. The thermoelectric power, measured for $Gd_3Co_6Sn_5$, and for comparison also for $Y_3Co_6Sn_5$ and $Er_3Co_6Sn_5$, is for each compound negative and of the order of several μV K^{-1} at room temperature.

1. Introduction

The formation of ternary stannides $RE_3Co_6Sn_5$ with RE = Y, Nd, Sm, Gd, Tb, Dy, Ho, Er and Tm was reported first by Pöttgen [1, 2], who also determined their crystal structures from the single-crystal x-ray data on $Sm_3Co_6Sn_5$ [1] and $Dy_3Co_6Sn_5$ [2]. All these compounds crystallize with a ternary ordered derivative of the La_3Al_{11}-type structure (space group $Immm$). To our knowledge, physical properties have been studied so far only for $Er_3Co_6Sn_5$.

[4] Author to whom any correspondence should be addressed.

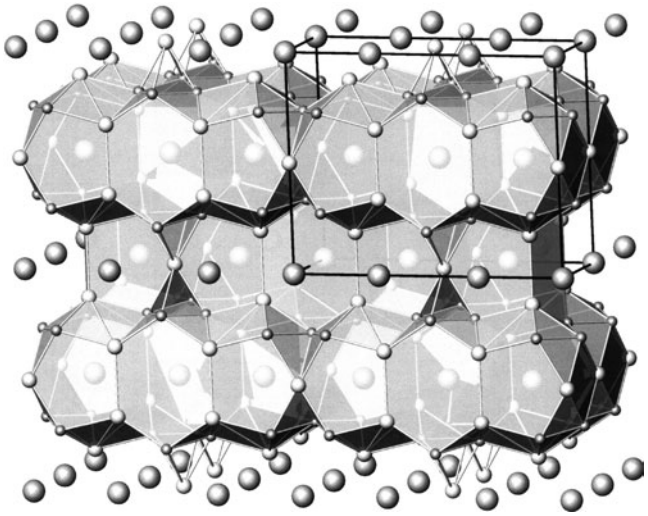

Figure 1. The crystal structure of $Gd_3Co_6Sn_5$ in a three-dimensional view (space group $Immm$; $Dy_3Co_6Sn_5$-type structure). Large circles: Gd atoms; medium circles: Sn atoms; small circles: Co atoms. The nearest-neighbour coordination polyhedra around the Gd atoms are shown. The unit cell is outlined by thin solid lines.

Skolozdra *et al* [3] measured the magnetic susceptibility of this compound down to 80 K and found a Curie–Weiss behaviour with $\theta_p = 9$ K. The electrical resistivity of $Er_3Co_6Sn_5$ was measured in the temperature interval 4.2–300 K by Dremov *et al* [4]. They reported finding metallic conductivity with some indication of a strong scattering of conduction electrons in the Co 3d-band states.

In this paper we report on the magnetic and electrical properties of $RE_3Co_6Sn_5$ phases with RE = Sm, Gd, Tb and Dy.

2. Experimental details

Polycrystalline samples of the $RE_3Co_6Sn_5$ compounds (RE = Sm, Gd, Tb and Dy) were prepared by arc-melting constituent elements in a titanium-gettered argon atmosphere and subsequently annealing the melted buttons in vacuum at 1073 K for ten days. After heat treatment the samples were checked by x-ray powder diffraction, which proved the single-phase character of all the alloys with the expected orthorhombic crystal structure. The refined lattice parameters were in good accordance with the literature data [1]. Figure 1 shows the crystal structure of the compounds in a three-dimensional view.

Magnetization and magnetic susceptibility measurements were carried out in the temperature range 1.7–300 K and in magnetic fields up to 5 T using a commercial SQUID magnetometer. The electrical resistivity was measured in the interval 4.2–300 K employing a conventional dc four-point technique. For $Dy_3Co_6Sn_5$ the resistivity measurements were extended down to 1.2 K. The thermoelectric power was measured in the temperature range 80–380 K using a standard differential method with pure copper as a reference material.

3. Results and discussion

The magnetic behaviour in $Sm_3Co_6Sn_5$ is summarized in figure 2. The pronounced minimum in $\chi^{-1}(T)$ clearly indicates that the compound orders antiferromagnetically at $T_N = 8$ K.

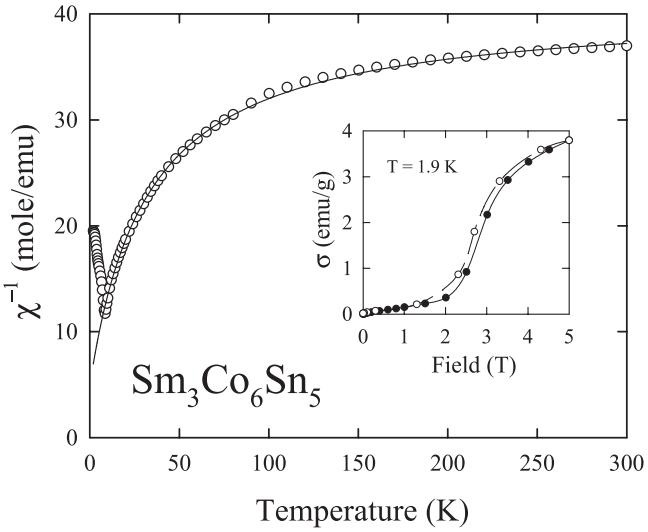

Figure 2. The temperature dependence of the reciprocal molar magnetic susceptibility of $Sm_3Co_6Sn_5$, measured in a field of 0.5 T. The solid curve represents a modified Curie–Weiss fit with the parameters given in the text. Inset: the field variation of the magnetization taken at $T = 1.9$ K with increasing (full circles) and decreasing (open circles) magnetic field.

The antiferromagnetic ground state is further corroborated by a distinct metamagnetic-like transition in the field-dependent magnetization that for $T = 1.9$ K has its onset in a field of about 2 T (see the inset to figure 2). In the paramagnetic region the inverse susceptibility is strongly curvilinear, as usually found for Sm-based compounds due to the closeness of the $^6H_{5/2}$ and $^6H_{7/2}$ terms in the Sm^{3+} ground multiplet [5]. The modified Curie–Weiss law applied to the magnetic data for $Sm_3Co_6Sn_5$ above 10 K yields the following parameters: the effective magnetic moment $\mu_{eff} = 1.36\ \mu_B$/Sm atom, the paramagnetic Curie temperature $\theta_p = -3.9$ K and the Van Vleck contribution $\chi_0 = 0.0246$ emu mol^{-1}.

In contrast to the case for $Sm_3Co_6Sn_5$, the inverse magnetic susceptibility of the compounds $RE_3Co_6Sn_5$ with RE = Gd, Tb and Dy shows a straight-line behaviour above about 30, 50 and 100 K, respectively (see figure 3). The effective magnetic moments μ_{eff} derived from the Curie–Weiss law amount to 8.07, 10.22 and 10.73 μ_B/RE atom, for $Gd_3Co_6Sn_5$, $Tb_3Co_6Sn_5$ and $Dy_3Co_6Sn_5$, respectively, thus being close to the theoretical values derived for free RE^{3+} ions (7.94, 9.72 and 10.65 μ_B, respectively). The corresponding paramagnetic Curie temperatures are equal to 20.7, 18.8 and −10.8 K, respectively. The positive θ_p-values found for both $Gd_3Co_6Sn_5$ and $Tb_3Co_6Sn_5$ hint at possible ferromagnetic properties at low temperatures, while the negative θ_p acquired for $Dy_3Co_6Sn_5$ possibly manifests antiferromagnetic exchange interactions.

The low-temperature behaviour of the magnetization in these three compounds is displayed in the insets to figure 3 and in figure 4. In accordance with the presumption based on the signs of θ_p, $Gd_3Co_6Sn_5$ and $Tb_3Co_6Sn_5$ order ferromagnetically at $T_C = 25$ and 16 K, respectively. For the Tb-based stannide a notable irreversibility is observed between the zero-field-cooled (ZFC) and field-cooled (FC) magnetization curves taken in a weak magnetic field (see the inset to figure 3(b)), which implies some magnetic anisotropy. Indeed, the field-dependent magnetization isotherms, measured at $T = 1.7$ K, exhibit a hysteretic behaviour with a remanence of about 60% of the saturation value σ_s that is of about 60 emu g^{-1} in $\mu_0 H = 5$ T

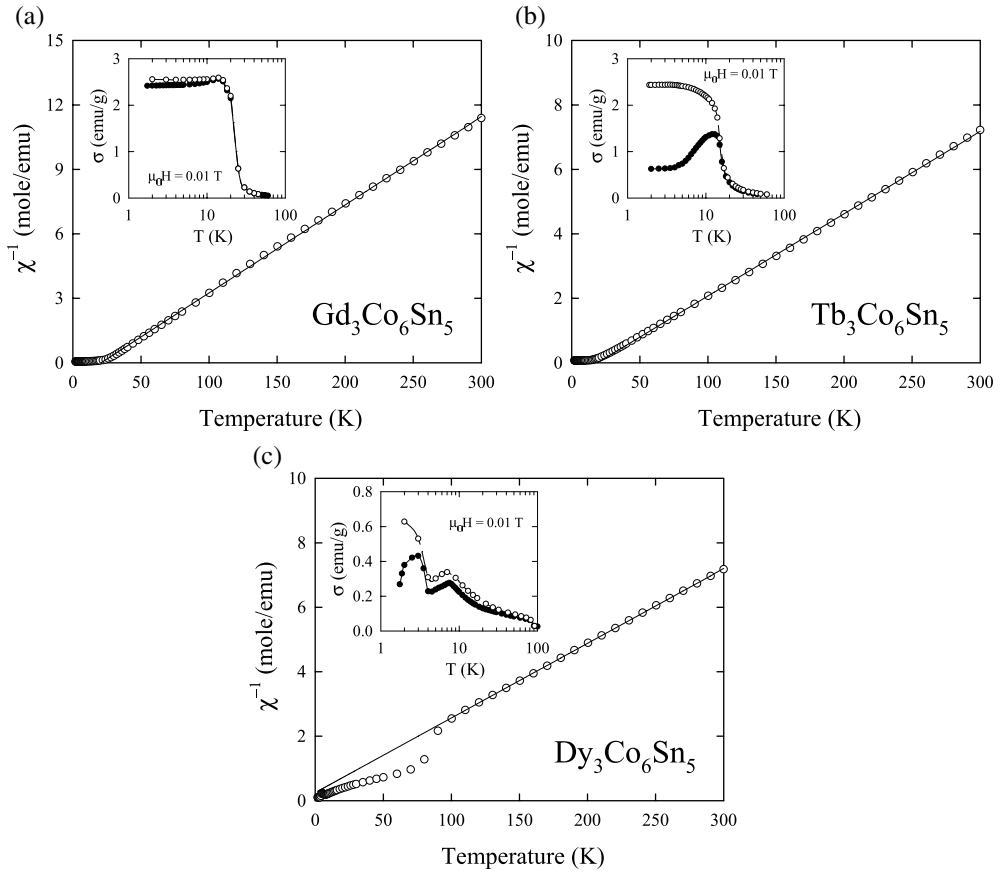

Figure 3. The temperature dependence of the reciprocal molar magnetic susceptibility of (a) $Gd_3Co_6Sn_5$, (b) $Tb_3Co_6Sn_5$, (c) $Dy_3Co_6Sn_5$, measured in a field of 0.5 T. Solid lines represent Curie–Weiss fits with the parameters given in the text. Insets: the low-temperature variation of the magnetization measured in a field of 0.01 T upon cooling the specimens in zero (full circles) and an applied (open circles) magnetic field.

(see figure 4(b)). With increasing temperature the hysteresis quickly diminishes and above 10 K it is already hardly perceivable. The aforementioned value of σ_s corresponds to the Tb magnetic moment $\mu_s = 5.11\ \mu_B$, which should be compared with the ordered moment of a free Tb^{3+} ion of 9 μ_B. This strong reduction in the magnetic moment measured presumably results from crystal field interactions.

The other ferromagnet, i.e. $Gd_3Co_6Sn_5$, shows more complex properties, undergoing in the ordered state another phase transition at $T_1 = 12$ K (see the inset to figure 3(a)). This feature may be interpreted in terms of reconstruction of the magnetic structure, e.g. due to canting in the Gd-moment sublattice. Alternatively, one should consider the possibility that also Co atoms may carry magnetic moments and below T_1 align antiparallel to the Gd moments. The latter hypothesis seems somewhat supported by the value of the saturated magnetization at $T = 1.7$ K and $\mu_0 H = 5$ T, which is 75 emu g^{-1} (see figure 4(a)), which corresponds to $\mu_s = 6.36\ \mu_B$, i.e. a bit smaller than the value characteristic of Gd^{3+} ions (7 μ_B). On the other hand, Dremov *et al* [4] did not find any anomaly in the temperature-dependent resistivity of $Y_3Co_6Sn_5$ and $Er_3Co_6Sn_5$, which would hint at a magnetic nature of the Co atoms in these two

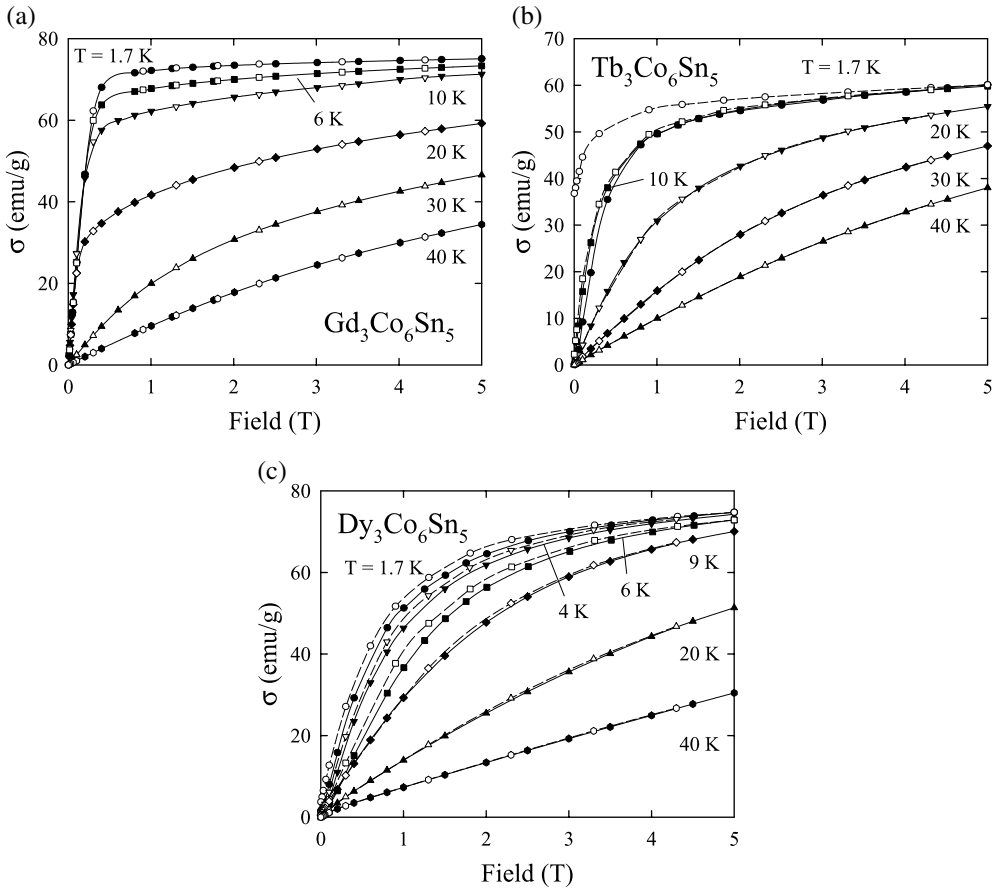

Figure 4. The field variation of the magnetization in (a) $Gd_3Co_6Sn_5$, (b) $Tb_3Co_6Sn_5$, (c) $Dy_3Co_6Sn_5$, measured at various temperatures below 40 K with increasing (full symbols) and decreasing (open symbols) magnetic field.

isostructural compounds, both appearing nonmagnetic down to 4.2 K. It is also worthwhile noting that for $Gd_3Co_6Sn_5$ almost no magnetic anisotropy is observed (note the very weak irreversibility in the $\sigma(T)$ variation and the absence of hysteresis in the $\sigma(H)$ isotherms), as expected for a system with an $L = 0$ ground state.

The most distinct feature in the inverse magnetic susceptibility of $Dy_3Co_6Sn_5$, displayed in figure 3(c), is a kink at about 80 K. It has a ferromagnetic-like character, but a small magnitude of the magnetization change near this temperature (see the inset to figure 3(c)) and an almost straight-line behaviour of the field-dependent magnetization isotherm taken at 40 K (compare figure 4(c)) both suggest that the observed transition may have extrinsic nature. Further support for this supposition comes from the fact that no anomaly is seen around 80 K in the temperature-dependent resistivity of $Dy_3Co_6Sn_5$ (see below and in figure 5(c)). In turn, the most likely impurity in the sample measured is $Dy_3Co_8Sn_4$, a compound that was reported by Canepa and Napoletano [6] to be ferrimagnetic below about 80 K. From a simple comparison of the $\sigma(T)$ data, shown in the inset to figure 3(c), with the $\sigma(T)$ results obtained for $Dy_3Co_8Sn_4$ by the latter authors (in a similar applied field of 0.01 T), one can estimate the concentration of the minority phase in the sample measured to be about 1.5%. Obviously, such a small amount of

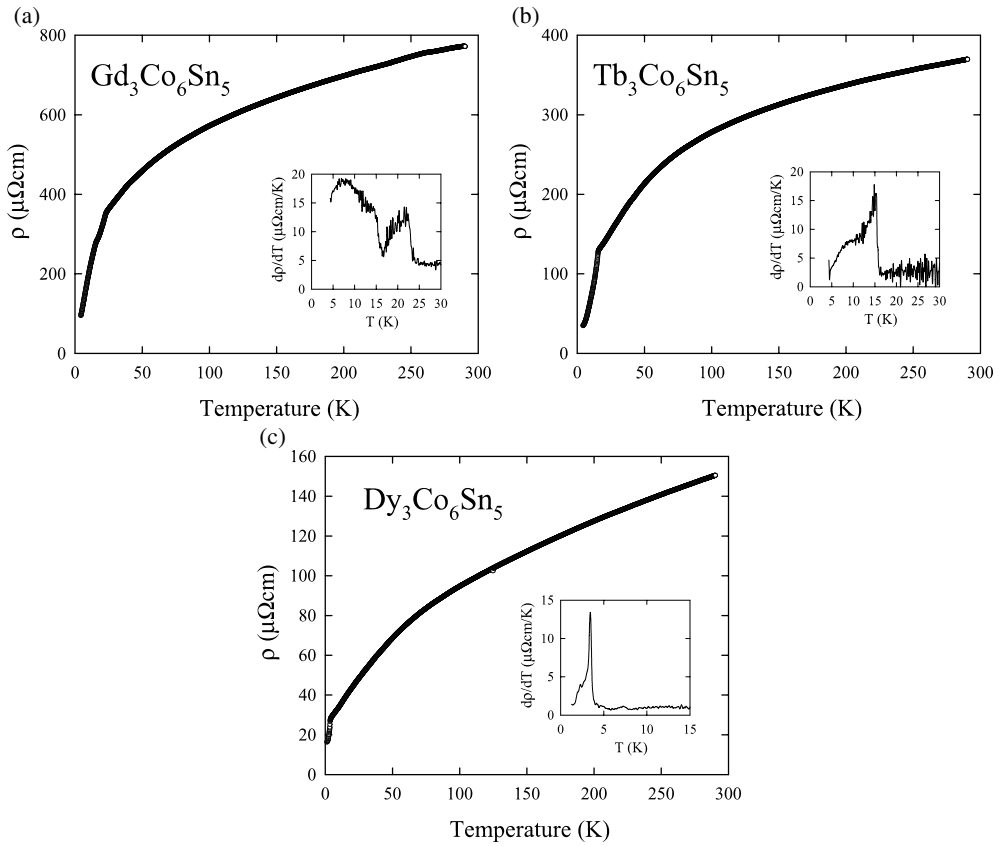

Figure 5. The temperature dependence of the electrical resistivity of (a) $Gd_3Co_6Sn_5$, (b) $Tb_3Co_6Sn_5$, (c) $Dy_3Co_6Sn_5$. Insets: the temperature derivative of the electrical resistivity in the vicinity of the magnetic phase transitions.

the $Dy_3Co_8Sn_4$ impurity could not be resolved in the x-ray powder diffraction pattern, which showed single-phase material.

Other pronounced features of the $\sigma(T)$ curves of $Dy_3Co_6Sn_5$ are a maximum at $T_N = 7$ K and a ferromagnetic-like anomaly at $T_1 = 3$ K (see the inset to figure 3(c)). It seems that the compound first undergoes a transition from a paramagnetic to an antiferromagnetic state, and then the magnetic structure alters, possibly in a manner suggested above for $Gd_3Co_6Sn_5$, i.e. for example involving some canting of primarily antiparallel magnetic moments. The magnetization $\sigma(B)$, measured at $T = 1.7$ K, shows in high fields a nearly saturated behaviour and in $\mu_0 H = 5$ T it reaches 75 emu g^{-1} (see figure 4(c)), which corresponds to $\mu_s = 6.40\ \mu_B$ per Dy atom. This latter value is much smaller in comparison to a Russell–Saunders ordered moment of Dy^{3+} ion ($10\ \mu_B$), and the difference is presumably caused by crystal field effects.

In figure 5 there are shown the temperature-dependent electrical resistivities of $Gd_3Co_6Sn_5$, $Tb_3Co_6Sn_5$ and $Dy_3Co_6Sn_5$. All three compounds exhibit the metallic type of conductivity. The magnitude of the resistivity measured at room temperature rapidly decreases along the series, being about 780 $\mu\Omega$ cm for the Gd-based stannide, 370 $\mu\Omega$ cm for $Tb_3Co_6Sn_5$ and only 150 $\mu\Omega$ cm for the Dy-containing phase. The residual resistivity ratio was for all samples of the order of 8. In the respective paramagnetic regions the $\rho(T)$ dependences are considerably

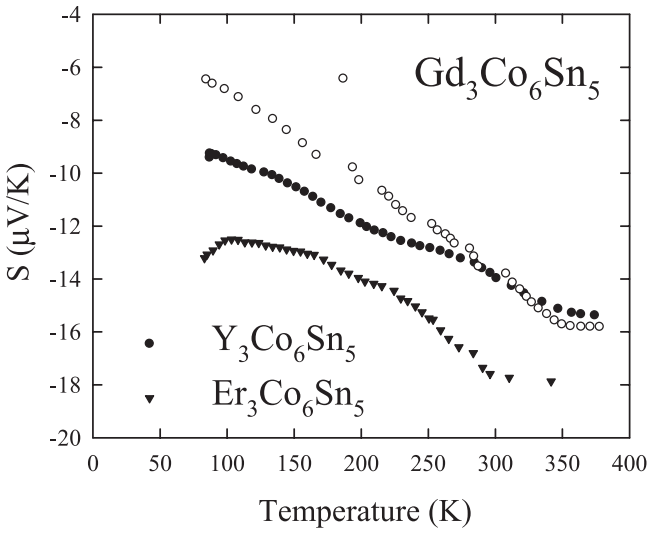

Figure 6. The temperature dependence of the thermoelectric power of $Y_3Co_6Sn_5$, $Gd_3Co_6Sn_5$ and $Er_3Co_6Sn_5$.

curvilinear, probably mainly because of the Mott–Jones-type scattering of the conduction electrons [7] related to the presence of the 3d band of cobalt. In the case of $Tb_3Co_6Sn_5$ and $Dy_3Co_6Sn_5$ another contribution due to spin-disorder scattering influenced by crystal field interaction has to be taken into account.

The magnetic phase transitions manifest themselves on the $\rho(T)$ curves as more or less pronounced kinks, and in the temperature derivatives of the resistivity as Fisher–Langer-type anomalies (see the insets to figure 5). For $Gd_3Co_6Sn_5$ two such features are apparent at $T = 15$ and 24 K, roughly in accordance with the magnetic data. In the case of $Tb_3Co_6Sn_5$ just one distinct anomaly occurs, at $T = 15$ K, which nicely corresponds to $T_C = 16$ K. Finally, for $Dy_3Co_6Sn_5$ a sharp kink in $\rho(T)$ and a prominent maximum in $\mathrm{d}\rho/\mathrm{d}T(T)$ are both observed at $T = 3$ K that can be unambiguously associated with the order–order magnetic phase transition revealed at this temperature in the magnetic studies. In turn, at the Néel temperature $T_N = 7$ K, only a tiny maximum is seen in $\mathrm{d}\rho/\mathrm{d}T(T)$ and hardly any anomaly in $\rho(T)$. It is also worthwhile noting that in the vicinity of 80 K both the temperature-dependent resistivity and its derivative are featureless, thus confirming the extrinsic nature of the irregularity found at this temperature in the magnetization.

The thermoelectric power, measured as a function of temperature for $Gd_3Co_6Sn_5$, is presented in figure 6. For comparison there are shown the $S(T)$ variations determined for $Y_3Co_6Sn_5$ and $Er_3Co_6Sn_5$. For all three compounds the Seebeck coefficient is negative, thus indicating the dominance of electronic-type conductivity. With rising temperature the absolute values of the thermopower slightly increase, arriving at 15–18 μV K^{-1} above room temperature. As is apparent from figure 6, the magnitude and the temperature dependences of the thermoelectric power of the two ternaries containing magnetic rare-earth atoms are very similar to those characterizing the Y-based compound. This finding implies a rather minor role of the RE constituents in the electronic transport of the $RE_3Co_6Sn_5$ stannides, at least in the paramagnetic state. In this region the electrical behaviour is probably governed mainly by the contribution due to Co atoms, i.e. it reflects the presence of relatively broad 3d bands in the density of states near the Fermi energy.

4. Summary

The magnetic and electrical properties were determined for a series of $RE_3Co_6Sn_5$ ternary stannides with RE = Sm, Gd, Tb and Dy. All these compounds are metallic and exhibit at low temperatures long-range magnetic ordering, that at least for Gd- and Dy-based materials may have a complex character. Subsequent phase transitions observed in these two phases presumably manifest reorientations of RE magnetic moments, yet the possibility of some interplay of magnetism related to cobalt atoms, although less likely, cannot be completely ruled out at the present stage. Neutron diffraction studies would be essential to solve this problem.

Acknowledgments

The present work was supported by the Polish State Committee for Scientific Research (grant KBN No 4 T08A 045 24), the Ukrainian Ministry of Education and Science (grant No 0100U001431) and the Austrian–Polish Scientific Technical Exchange Programme.

References

[1] Pöttgen R 1995 *J. Alloys Compounds* **224** 14
[2] Pöttgen R 1995 *Z. Naturf.* b **50** 175
[3] Skolozdra R V, Mudryk Ya S and Romaka L P 2000 *J. Alloys Compounds* **296** 290
[4] Dremov R V, Koblyuk N, Mudryk Ya S, Romaka L P and Sechovsky V 2001 *J. Alloys Compounds* **317/318** 293
[5] Taylor K N R and Darby M I, 1972 *Physics of Rare Earth Solids* (London: Chapman and Hall)
[6] Canepa F and Napoletano M 2001 *J. Alloys Compounds* **325** L4
[7] Mott N F and Jones H 1958 *The Theory of the Properties of Metals and Alloys* (London: Oxford University Press)