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The transport properties of RCo₂ compounds

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Abstract. The transport properties of intermetallic compounds RCo₂ (R = Pr, Nd, Sm, Gd–Lu, Sc and Y) in the temperature range from 4.2 up to 1000 K were studied and different contributions were determined. In the non-magnetic compounds the spin fluctuation contribution to the electrical resistivity, $\rho_{sf} \propto (T/T_{sf})^2$, and thermal resistivity, $W_{sf} \propto (T/T_{sf})$, were found to follow the theoretical predictions. The spin disorder contribution arising from the scattering of conduction electrons on 4f moments was deduced and found to be proportional to the de Gennes factor. It is shown that the spin fluctuations are responsible for the low-temperature features of the temperature-dependent thermopower, whereas the high-temperature behaviour is mainly determined by the density of states function.

In the paramagnetic region near the Curie temperature, the critical fluctuations cause a considerable enhancement of the electrical resistivity of the magnetic RCo₂ compounds, which is manifested by pronounced upturns in ρ versus T dependences.

1. Introduction

The rare earth (RE) cubic Laves phases with cobalt (RCo₂) are of particular interest because of their outstanding magnetic properties associated with the itinerant d-electron subsystem [1, 2, 3]. Within this series, YCo₂, LuCo₂ and ScCo₂ are exchange-enhanced itinerant paramagnets, whereas compounds with magnetic RE are ferro- or ferrimagnets depending on whether they contain light (Pr, Nd, Sm) or heavy (Gd to Tm) RE metals. In magnetic RCo₂ compounds, long-range magnetic order is induced in the itinerant d-electron subsystem by the ordered localized RE moments. The magnetic phase transition is of first-order type in RCo₂ with R = Tm, Er, Ho and Dy, while it is of second-order type in the others [3].

Calculations of the density of states, $N(\varepsilon)$, for YCo₂ [4, 5, 6] revealed the importance of the 3d–4d (3d–5d in the case of lanthanides) hybridization in forming the d-band structure of these Laves phases (it is assumed that $N(\varepsilon)$ has the same general features throughout the RCo₂ series). According to these calculations, the Fermi level, ε_F , lies near a sharp peak in $N(\varepsilon)$ caused mainly by the 3d states. Many striking properties of the RCo₂ compounds, such as the itinerant metamagnetism and enhanced electronic specific heat coefficient observed in YCo₂ and LuCo₂ and the first-order magnetic phase transitions in the magnetic RCo₂ compounds, were related to these features. However, in order to explain the temperature variation of the transport properties the collective excitations in the highly correlated d-electron subsystem have to be taken into account.

It has been shown that spin fluctuations can significantly influence the temperature variation of the electrical resistivity of paramagnetic RCO_2 [7]. This seems to be plausible, since the question of whether these collective excitations can be observed in an experiment depends on their characteristic time scale and the characteristic time of the experiment used. An estimation of the characteristic time scale of transport phenomena gives about 10^{-14} s, which is of the same order as the time scale of spin fluctuations, τ_{sf} , in the d-electron system [8]. In case of the magnetic RCO_2 compounds the spin fluctuations influence the transport properties only in the paramagnetic state, since below T_C they are suppressed, thus giving rise to huge anomalies at T_C in the $\rho(T)$ dependences [7].

In order to show the effect of spin fluctuations on the transport properties a correct separation of different scattering contributions, usually based on the validity of Matthiessen's rule, is necessary. For the non-magnetic RCO_2 compounds the total electrical resistivity $\rho(T)$ and accordingly the electronic thermal resistivity $W_{el}(T) = \lambda_{el}^{-1}(T)$ can be written as

$$\rho(T) = \rho_0 + \rho_{ph}(T) + \rho_{sf}(T) \quad (1)$$

and

$$W_e(T) = W_{e,0} + W_{e,ph} + W_{e,sf} \quad (2)$$

where the subscripts 0, *ph* and *sf* denote the contributions due to impurity, phonon and spin fluctuation scatterings, respectively; the subscript *e* in equation (2) indicates the electronic part of the thermal resistivity. For the thermopower, no such simple relation exists, although in some cases Kohler's rule or the Norheim-Gorter rule can be applied for the data analysis [12, 13]. All these rules are based on the assumption that the different scattering processes are independent, which is however not always the case.

Theoretical calculations concerning the influence of spin fluctuations on the transport properties mainly deal with the low-temperature limit. Coqblin *et al* in [9] and later Moriya in [10] extended the calculations to high temperatures. It was found that at low temperatures, the spin fluctuations affect the scattering in much the same way as damped phonons do. This contribution is strongly temperature dependent with a tendency to saturate at elevated temperatures. The temperature above which this crossover occurs is determined by the so called spin fluctuation temperature, T_{sf} . In nearly ferromagnetic systems, which are of particular interest for this study, only collective fluctuations with small wavevector are important in the spectral distribution. For this long-wavelength approximation, explicit expressions for the temperature variation of the transport properties have been derived [9, 10]. In the following the most important results are summarized.

Low temperatures, $T < T_{sf}$:

Electrical resistivity: $\rho_{sf} = AT^2$, with *A* proportional to T_{sf}^{-2} .

Magnetoresistance: $(\Delta\rho/\rho)_{sf}$ is negative and proportional to the square of the applied magnetic field.

Thermal resistivity: $W_{sf} = cT$, with *c* proportional to T_{sf}^{-1} .

Thermopower: the situation is not yet clear. In some calculations a minimum below T_{sf} has been predicted [11].

Elevated temperatures:

Electrical resistivity: ρ_{sf} saturates somewhat above T_{sf} . According to [9], for high values of the Stoner enhancement factor the resistivity can go through a maximum above T_{sf} followed by a negative slope towards the high-temperature region.

Thermal resistivity: W_{sf} passes a maximum around T_{sf} and decreases proportional to T^{-1} at higher temperatures.

In this paper we analyse various transport properties of magnetic and non-magnetic $R\text{Co}_2$ compounds in the framework of the above described concepts. We summarize our earlier published experimental data on the low-temperature electrical resistivity and thermoelectric power of the $R\text{Co}_2$ intermetallic compounds [14] and additionally new data on the resistivity and thermopower in the temperature region from 300 K to 1000 K are presented. The thermal conductivity of YCo_2 , LuCo_2 and ScCo_2 from 4.2 K to 300 K was measured and the experimental data are discussed. As will be shown, the high-temperature measurements are necessary for a better understanding of the spin fluctuation scattering processes in those compounds.

2. Experimental details

Samples of $R\text{Co}_2$ with $R = \text{Pr}, \text{Nd}, \text{Sm}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{Lu}, \text{Sc}$ and Y were melted in an induction furnace under a protective argon atmosphere and subsequently annealed, under vacuum conditions for about one week at 1070 K. The compounds with $R = \text{Ce}, \text{La}, \text{Eu}$ and Yb either could not be obtained with satisfactory phase purity, or we failed in our attempts to prepare them. X-ray analysis showed traces of the $R\text{Co}_3$ phase in PrCo_2 and NdCo_2 (below 5%).

A four-probe dc method was used for the electrical resistivity measurements; for the thermopower measurements a differential method was applied. Typical sizes of the samples were about $1 \times 1 \times 10 \text{ mm}^3$. The estimated error in the absolute value of the electrical resistivity is $\pm 5\%$. This is mainly due to uncertainty in the sample geometry which is closely related to the mechanical quality of the samples. The thermopower was measured with an accuracy of about $\pm 0.5 \mu\text{V K}^{-1}$. For the thermal conductivity experiments, a constant temperature gradient of about 1% of the measuring temperature was produced using a strain gauge as a heater. The produced temperature difference was measured by differential thermocouples. Half-cylindrical samples with about 30 mm in length and 4 mm in diameter were used for these experiments.

3. Results and discussion

3.1. Paramagnetic compounds ScCo_2 , YCo_2 and LuCo_2

The electrical resistivity and thermopower of the non-magnetic Laves phases have been studied by several groups mainly at low temperatures (see, e.g., [14, 15, 16]), whereas the thermal conductivity data are known only for the RAl_2 cubic Laves phase compounds [17].

3.1.1. Electrical resistivity. The temperature dependence of the electrical resistivity of YCo_2 , LuCo_2 and ScCo_2 is shown in figure 1. The residual resistivity ρ_0 has been subtracted in this figure and the values are listed in table 1. To demonstrate the influence of the spin fluctuation scattering in these compounds, $\rho(T)$ of the two isostructural non-spin fluctuation intermetallics YAl_2 and LuNi_2 is also given in this figure. Assuming that the phonon induced resistivity, $\rho_{ph}(T)$, is essentially the same among these RT_2 Laves phases, YAl_2 (or LuNi_2) can be used to determine the spin fluctuation contribution, $\rho_{sf}(T)$, to the total resistivity within the scope of Matthiessen's rule. For this purpose we subtracted the $\rho(T)$ curve of YAl_2 from those of YCo_2 , LuCo_2 and ScCo_2 . Figure 2 shows the temperature variation of the spin fluctuation contribution to the total resistivity of YCo_2 , LuCo_2 and ScCo_2 . As can be seen, $\rho_{sf}(T)$ is characterized by the following features:

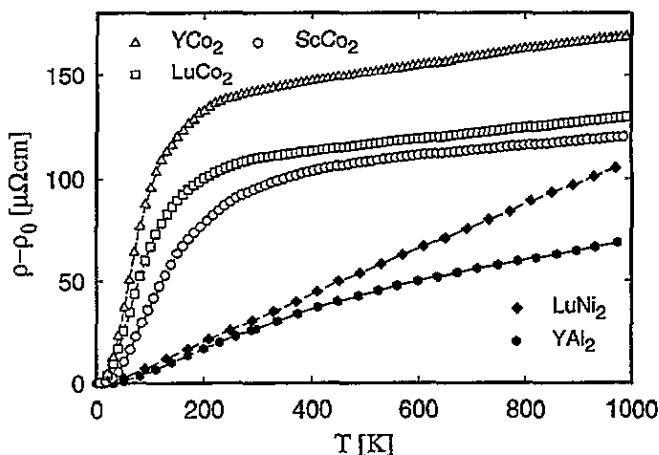


Figure 1. Temperature dependence of the electrical resistivity of the spin fluctuation systems YCo_2 , LuCo_2 and ScCo_2 . For comparison the resistivity of the isostructural non-spin fluctuation compounds YAl_2 and LuNi_2 is shown. The respective residual resistivities ρ_0 are listed in table 1.

Table 1. Characteristic parameters of the RCo_2 intermetallic compounds. ρ_0 denotes the residual resistivity determined at 4.2 K, T_C is the Curie temperature deduced from $d\rho/dT$ and ρ_{spd} gives the spin disorder resistivity.

Compound	ρ_0 ($\mu\Omega$ cm)	T_C (K)	ρ_{spd} ($\mu\Omega$ cm)
PrCo_2	20	39	16
NdCo_2	30	98	8
SmCo_2	3	203	45
GdCo_2	3	390	41
TbCo_2	12	233	31
DyCo_2	4	136	25
HoCo_2	9	77	16
ErCo_2	11	31	10
TmCo_2	4	3.9	16
ScCo_2	18	—	—
LuCo_2	24	—	—
YCo_2	17	—	—

(i) A steep increase at low temperatures followed by a maximum is observable in all the $\rho_{sf}(T)$ curves.

(ii) The position of the maximum is different for the three compounds studied: 220 K (YCo_2), 250 K (LuCo_2) and 330 K (ScCo_2).

(iii) At high temperatures $\rho_{sf}(T)$ decreases nearly linearly with increasing temperature.

The same variation of ρ_{sf} with the temperature is observable irrespective of which reference material has been used. However, the decrease in $\rho_{sf}(T)$ is more pronounced when RNi_2 is used for the subtraction of $\rho_{ph}(T)$. One curve in figure 2 demonstrates the temperature variation of $\rho_{sf}(T)$ for LuCo_2 if LuNi_2 is used to eliminate the phonon contribution.

A detailed analysis shows that the spin fluctuation part of the resistivity depends quadratically on T at low temperatures ($\rho_{sf} = AT^2$); this is shown in figure 3. The

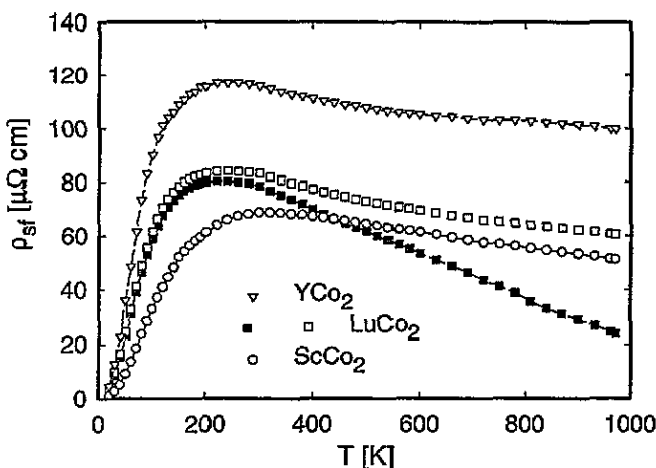


Figure 2. Temperature dependence of the spin fluctuation resistivity of YCo_2 , LuCo_2 and ScCo_2 . ∇ : $(\rho(T) - \rho_0)_{\text{YCo}_2} - (\rho(T) - \rho_0)_{\text{YAl}_2}$ \square : $(\rho(T) - \rho_0)_{\text{LuCo}_2} - (\rho(T) - \rho_0)_{\text{YAl}_2}$ \blacksquare : $(\rho(T) - \rho_0)_{\text{LuCo}_2} - (\rho(T) - \rho_0)_{\text{LuNi}_2}$ \circ : $(\rho(T) - \rho_0)_{\text{ScCo}_2} - (\rho(T) - \rho_0)_{\text{YAl}_2}$.

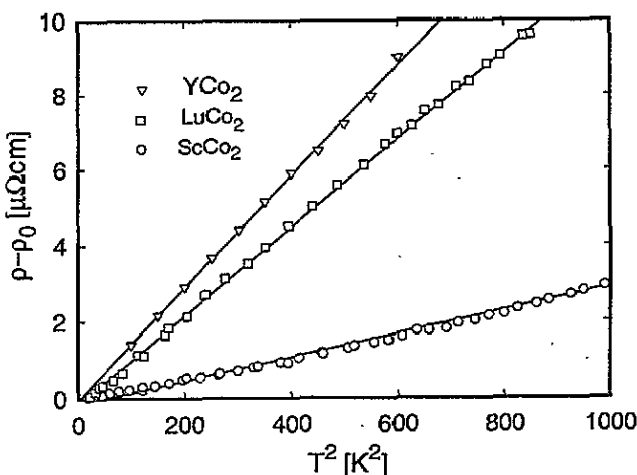


Figure 3. Low-temperature spin fluctuation part of the resistivity of YCo_2 , LuCo_2 and ScCo_2 as a function of T^2 ($\rho_{sf}(T) = AT^2$). Solid straight lines are drawn with $A(\text{YCo}_2) = 16$ ($\text{n}\Omega \text{ cm K}^{-2}$), $A(\text{LuCo}_2) = 12$ ($\text{n}\Omega \text{ cm K}^{-2}$) and $A(\text{ScCo}_2) = 4.3$ ($\text{n}\Omega \text{ cm K}^{-2}$).

corresponding A/γ ratios (where γ is the coefficient of the electronic specific heat measured on the same samples [18]) for these compounds are of the order of about 10^{-5} ($\mu\Omega \text{ cm K}^2 \text{ mol}^2 \text{ mJ}^{-2}$). These values fit well into the region for spin fluctuation compounds in the so-called Kadowaki–Woods plot [19] (figure 4).

3.1.2. Thermopower. The temperature variation of the thermopower of YCo_2 , LuCo_2 and ScCo_2 is presented in figure 5 together with that of YAl_2 . We note that the S versus T dependences of the spin fluctuation compounds and YAl_2 are qualitatively similar. The $S(T)$ curves are characterized by two minima: one at low temperature around 20–40 K and

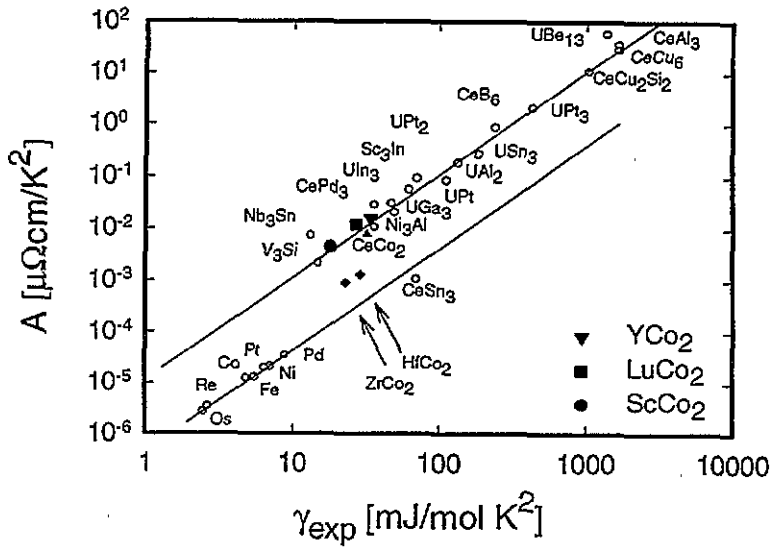


Figure 4. Position of the three spin fluctuation systems YCo_2 , LuCo_2 and ScCo_2 within the Kadowaki-Woods plot [19].

the second, essentially broadened, above 200 K: 205 K (YCo_2), 290 K (LuCo_2), 390 K (ScCo_2) and 490 K (YAl_2). However, the absolute S -values of the spin fluctuation systems are substantially larger and both minima are much deeper.

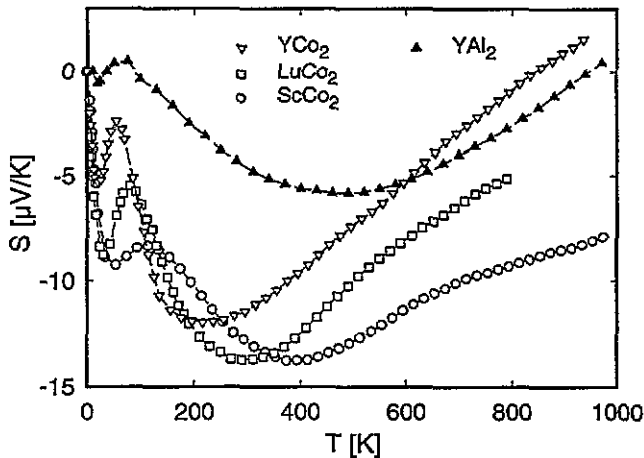


Figure 5. Temperature dependence of the thermopower of YCo_2 , LuCo_2 and ScCo_2 . S versus T of the isostructural non-spin fluctuation system YAl_2 is included for comparison.

The low-temperature minimum in YAl_2 has been referred to as the 'phonon-drag' effect [20, 21]. To explain the low-lying deeper minimum in spin fluctuation systems, Fournier and Gratz [7] discussed the existence of a 'paramagnon-drag' effect. Similarly to the phonon-drag effect [12], it is assumed that in the presence of thermal non-equilibrium the paramagnons are able to drag charge carriers along the temperature gradient. This 'drag' contribution is strongly temperature dependent and, as in case of the phonon drag, disappears

quickly with increasing temperature due to a strengthening of thermal excitations within the spin fluctuation system.

The high-temperature minimum is of different origin. Coqblin *et al* [9] showed that 'uniform' spin fluctuations have only a small influence on the temperature variation of the thermopower. According to the arguments given in [9], the density of state properties at the Fermi level are much more important for the diffusion thermopower. Previously we have shown that at high temperatures the thermopower of La_xY_{1-x}Al₂ is mainly determined by the density of state features near ε_F , whereas the various scattering processes hardly influence $S(T)$.

Generally the diffusion thermopower can be expressed by [21]

$$S(T) = -\frac{1}{eT} \frac{\int_0^{\infty} \sigma(\varepsilon, T)(\varepsilon - \mu)(-\partial f^0/\partial \varepsilon) d\varepsilon}{\int_0^{\infty} \sigma(\varepsilon, T)(-\partial f^0/\partial \varepsilon) d\varepsilon} \quad (3)$$

Here $\sigma(\varepsilon, T)$ is the so-called spectral electrical conductivity, μ the chemical potential and $\partial f^0/\partial \varepsilon$ the derivative of the unperturbed Fermi distribution function f^0 . Assuming that the transition probabilities for the various scattering mechanisms are independent, we can describe the resulting spectral conductivity $\sigma(\varepsilon, T)$ as

$$\frac{1}{\sigma(\varepsilon, T)} = \sum_i \frac{1}{\sigma_i(\varepsilon, T)} \quad (4)$$

where the subscript i denotes the various scattering processes. Assuming furthermore that $\sigma_i(\varepsilon, T)$ can be written as

$$\sigma_i(\varepsilon, T) = \Lambda_i(T) \phi_i(\varepsilon) \quad (5)$$

and the $\phi_i(\varepsilon)$ functions are proportional to each other ($\phi_i = \text{constant} \phi_j$), $\Lambda_i(T)$ vanishes in the general expression for the thermopower with the consequence that the expression for the total thermopower reduces to that with only one scattering mechanism (for more details see [21]). It follows therefore that additional scattering mechanisms do not change the temperature dependence of the thermopower. As will be seen later, the temperature-dependent thermopower of the magnetic RCo₂ compounds in the paramagnetic temperature region, where an additional scattering mechanism caused by the localized 4f moments of RE exists, shows the same characteristic features as that of the paramagnetic RCo₂ compounds. This is most clearly seen in the case of TmCo₂ where the magnetic ordering is very low.

A closer inspection of the $S(T)$ curves given in figure 5 shows that there is a linear relation between the respective γ -value and the position of the high-temperature thermopower minimum. This relation is shown in figure 6. In our earlier analysis of $S(T)$ of YCo₂ [16] we argued that the position of the high-temperature minimum is determined by the width of the density of states function peak near ε_F . The correlation shown in figure 6 confirms this interpretation, since, following the arguments of Ikeda *et al* [23], the increasing lattice constant from ScCo₂ towards YCo₂ is responsible for a narrowing of the d band and thus for the increase of the γ value.

3.1.3. Thermal conductivity. The temperature variation of the thermal conductivity, λ , is given in figure 7. At elevated temperatures the three spin fluctuation systems show a thermal conductivity about half of that of YAl₂. Furthermore, there is much stronger curvature in λ versus T in the Co compounds observable in the low-temperature region.

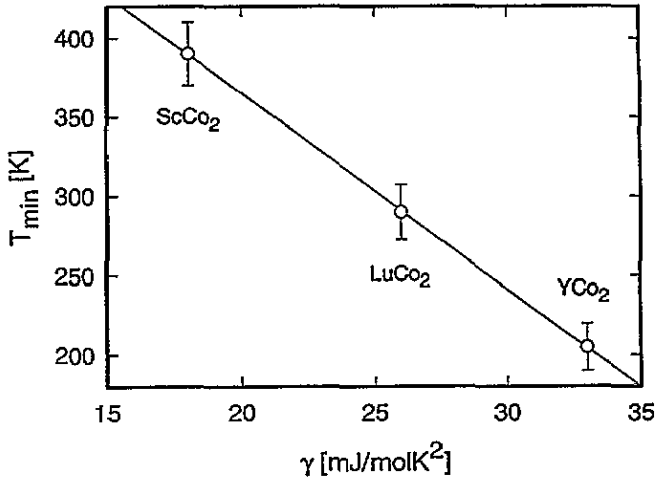


Figure 6. Linear relation between the high-temperature minimum in S versus T and the coefficient of the electronic specific heat γ .

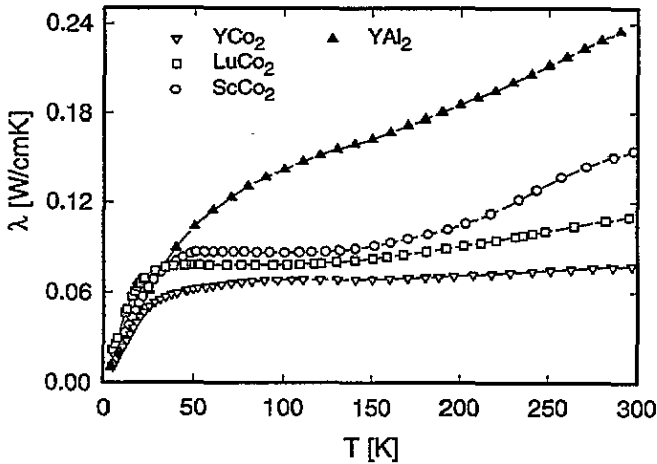


Figure 7. Temperature dependence of the thermal conductivity λ of the three spin fluctuation systems YCo₂, LuCo₂ and ScCo₂. For comparison the data of YAl₂ are also shown.

Using the theoretically predicted temperature dependences for different scattering contributions [9, 24, 25], we can account for the variation of $\lambda(T)$ at low temperatures. Assuming that the total thermal conductivity is a sum of the electronic and lattice contributions one gets from equation (2)

$$\lambda = (W_{e,0} + W_{e,ph} + W_{e,sf})^{-1} + \lambda_l. \tag{6}$$

Then, with $W_{e,0} \propto T^{-1}$, $W_{e,ph} \propto T^2$ and $\lambda_l \propto T^2$ we finally obtain

$$\lambda = (aT^{-1} + bT^2 + cT)^{-1} + dT^2. \tag{7}$$

Least-squares fits according to (7) are given by the solid lines in figure 8. The values obtained for the parameter c in (7) are: $c(\text{ScCo}_2) = 11 \times 10^{-5}$, $c(\text{LuCo}_2) = 21 \times 10^{-5}$ and $c(\text{YCo}_2) = 23 \times 10^{-5}$ in units of cm mW^{-1} . Equation (7) applied for treating $\lambda(T)$

of YAl₂ gives a value of c which is two orders of magnitude smaller compared to the Co compounds. Thus, the much stronger negative curvature in λ versus T of the Co compounds below 50 K is due to the spin fluctuation scattering described by the term cT , while the spin fluctuations are negligible in YAl₂.

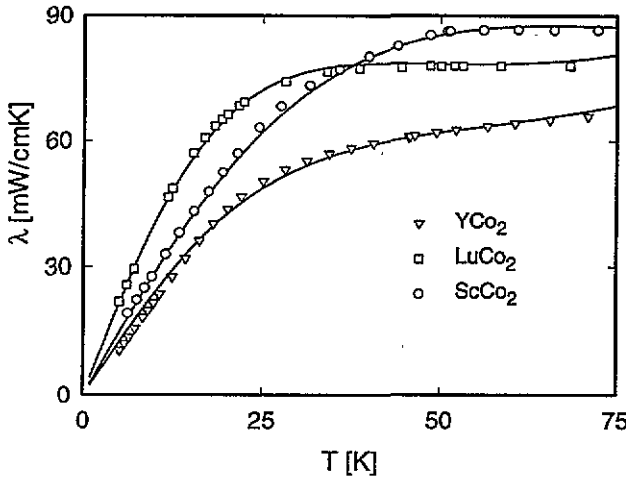


Figure 8. Least-squares fits according to (7) to the thermal conductivity data of YCo₂, LuCo₂ and ScCo₂.

The normalized Lorenz number

$$\frac{L}{L_0} = \frac{1}{L_0} \frac{\lambda_{el} \rho}{T} \quad (8)$$

(where λ_{el} is the electronic contribution to the thermal conductivity, ρ the electrical resistivity and L_0 the theoretical value of the Lorenz number for the free electron gas: $2.45 \times 10^{-8} \text{ W } \Omega \text{ K}^{-2}$) shows a strong temperature dependence with a maximum between 80 and 100 K; this is the temperature region where the strongest increase in ρ versus T was observed. The maximal value of L/L_0 is about three. The temperature dependence and the larger values of L/L_0 are caused by the circumstance that in the RCo₂ compounds different scattering mechanisms contribute in a different way to the electrical and thermal resistivity. It seems that the spin fluctuation scattering causes the deviation of L/L_0 from unity.

As already mentioned in the introduction, the spin fluctuation temperature is an important characteristic parameter for spin fluctuation systems. It is obvious that as T_{sf} decreases, the more pronounced is the influence of spin fluctuations on various physical quantities. However, the determination of the spin fluctuation temperatures from the transport data is difficult, since the parameters A (electrical resistivity) and c (thermal resistivity) are not directly proportional. From the ratio $[A(\text{YCo}_2)]^{1/2} : [A(\text{LuCo}_2)]^{1/2} : [A(\text{ScCo}_2)]^{1/2} \propto c(\text{YCo}_2) : c(\text{LuCo}_2) : c(\text{ScCo}_2)$ it follows that $T_{sf}(\text{YCo}_2) < T_{sf}(\text{LuCo}_2) < T_{sf}(\text{ScCo}_2)$.

It has been suggested to determine T_{sf} from the maximum in $d\rho/dT$; however there is no theoretical justification compared with the method we used in order to determine the ratio of T_{sf} . As seen from table 2, the ratios determined from $d\rho/dT$ differ essentially from the ratios given in the first two columns. We note that the values of T_{sf} estimated from specific heat data ($T_{sf}(\text{YCo}_2) = 40 \text{ K}$, $T_{sf}(\text{LuCo}_2) = 18 \text{ K}$ and $T_{sf}(\text{ScCo}_2) = 23 \text{ K}$ [23]) are in contrast to the sequence we found.

Table 2. Spin fluctuation temperature ratios estimated from different measurements.

	Thermal resistivity:	Electrical resistivity:	$\frac{d\rho}{dT}$:
	$\frac{T_{sf}^{(1)}}{T_{sf}^{(2)}} = \frac{\sigma_2}{c_1}$	$\frac{T_{sf}^{(1)}}{T_{sf}^{(2)}} = \sqrt{\frac{A_2}{A_1}}$	$\frac{T_{sf}^{(1)}}{T_{sf}^{(2)}} = \frac{T_{(d\rho_1/dT)_{max}}}{T_{(d\rho_2/dT)_{max}}}$
$\frac{\text{LuCo}_2}{\text{YCo}_2}$	1.1	1.2	1.1
$\frac{\text{ScCo}_2}{\text{YCo}_2}$	2.1	2.2	1.2
$\frac{\text{ScCo}_2}{\text{LuCo}_2}$	1.9	1.6	1.1

Finally we mention that the spin fluctuations we are discussing in connection with the transport data are thermal induced spin fluctuations within a narrow band. The role of the zero-point quantum fluctuations in the transport phenomena, which may also exist, is however not yet clear [10, 26]. There is evidence that these fluctuations also can show a temperature dependence and thus can influence transport properties, too [27].

3.2. Magnetic RCo₂ compounds

The RCo₂ compounds where the RE ions bear magnetic moments are of special interest, since one can study the influence of the molecular field (caused by the ordered RE 4f moments) on the spin fluctuations. It is known from many experiments that below T_C in the magnetic RCo₂ compounds, an induced Co moment of roughly $1 \mu_B$ appears and simultaneously the spin fluctuations vanish [2, 7]. This allows us to study the influence of the spin fluctuations on the transport phenomena in more detail, since the fluctuations within the magnetic d-electron subsystem are 'switched off' below T_C .

The electrical resistivity of some magnetic RCo₂ compounds (R = Gd, Tb, Dy, Ho and Er) was studied by Gratz *et al* [28] and Duc *et al* [29] in the temperature range from 4.2 K to 300 K. The resistivity of GdCo₂ was measured by Kawatra *et al* [30] in a limited temperature range around the Curie temperature. Recently, a detailed study of the resistivity of TmCo₂ as well as of Tm_{1-x}Gd_xCo₂ alloys was performed [31]. Among the RCo₂ intermetallics with light RE (Ce, Pr, Nd and Sm) only for NdCo₂ are the resistivity data in the region up to 300 K known in the literature [32]. The temperature-dependent thermopower of the heavy RCo₂ intermetallics in the low-temperature region up to 300 K was reviewed in [7]. No thermopower data for the light RCo₂ compounds are available in the literature.

3.2.1. Electrical resistivity. The temperature-dependent electrical resistivity for the three light RCo₂ compounds is shown in figure 9. As in figure 1, the residual resistivity has been subtracted in this representation; the values are given in table 1 (the enhanced ρ_0 values for the Pr and Nd compounds result probably from small RCo₃ impurities (see section 2)). In the ferromagnetic state, $\rho(T)$ is characterized by an extremely steep increase with increasing temperature followed by a flat and linear increase beyond room temperature.

The resistivity ($\rho - \rho_0$) of the heavy RCo₂ compounds is given in figures 10 and 11. For DyCo₂ the detailed ρ versus T curve around T_C , which illustrates the first-order phase transition, is given as an inset in figure 10. The inset in figure 11 represents $\rho(T)$ of TmCo₂ around the Curie temperature ($T_C = 3.9$ K). The hysteresis below T_C is caused by a 4f-spin rearrangement at 3.4 K [31]. Spin reorientations have also been observed in the

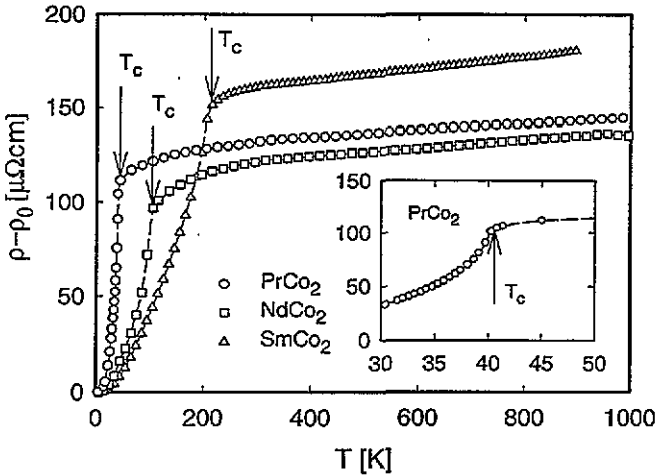


Figure 9. Temperature dependence of the electrical resistivity of $PrCo_2$, $NdCo_2$ and $SmCo_2$. The inset shows details of ρ versus T around T_C for $PrCo_2$.

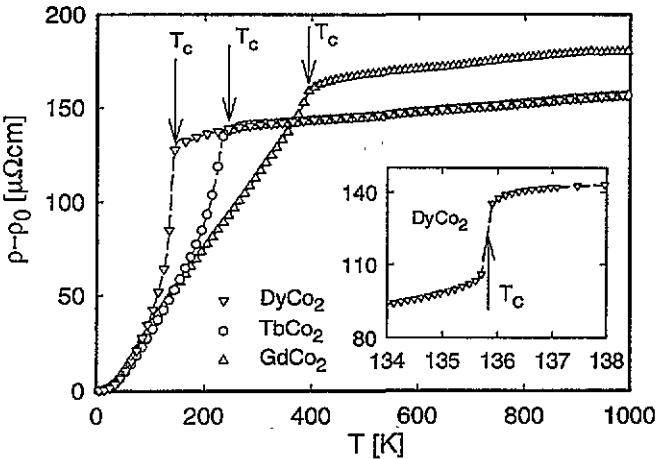


Figure 10. Temperature dependence of the electrical resistivity of $GdCo_2$, $TbCo_2$ and $DyCo_2$. The inset shows details of ρ versus T around T_C for $DyCo_2$.

electrical resistivity measurements in $HoCo_2$ and $NdCo_2$ [32]. As in the case of light RCO_2 , these $\rho(T)$ curves steeply increase in the ordered state, showing a characteristic kink at T_C , and saturate above about room temperature. Because of the first-order magnetic phase transition, the $\rho(T)$ curves for $DyCo_2$, $HoCo_2$ and $ErCo_2$ show a discontinuity at T_C . In $ErCo_2$, the resistivity drops by a factor of six at T_C within a few tenths of a degree. The Curie temperatures of the studied compounds deduced from $d\rho/dT$ are indicated by arrows and are collected in table 1. Both for the light and for the heavy RCO_2 compounds, they agree well with those given in the literature [2].

To obtain the influence of the magnetic $4f$ ions on the spin fluctuations in the Co d-electron subsystem, we again used Matthiessen's rule. The total resistivity of a magnetic

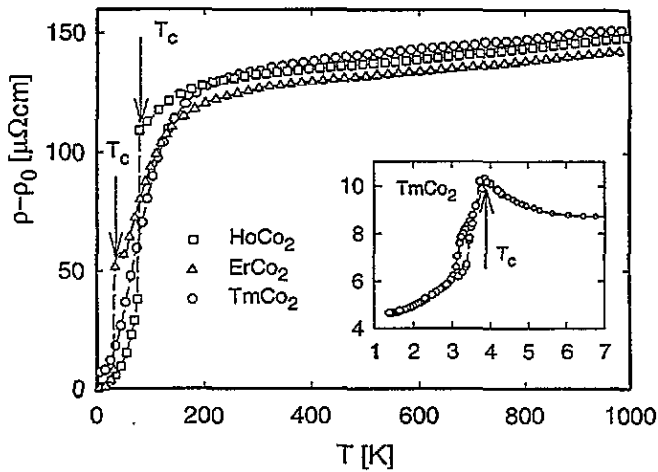


Figure 11. Temperature dependence of the electrical resistivity of HoCo_2 , ErCo_2 and TmCo_2 . The inset shows details of ρ versus T around T_C for TmCo_2 .

compound can be written as:

$$\rho(T) = \rho_0 + \rho_{ph}(T) + \rho_{mag}(T). \quad (9)$$

We assume that in the paramagnetic state $\rho_{mag}(T)$ consists of two contributions caused by the scattering of conduction electrons on 4f moments, usually called the spin disorder contribution $\rho_{spd}(T)$, and on spin fluctuations, $\rho_{sf}(T)$. The spin disorder contribution is expected to be temperature independent and proportional to the de Gennes factor $(g-1)^2 J(J+1)$ [33]. This proportionality was experimentally confirmed for the isostructural Laves phases RAl_2 and RNi_2 with heavy RE and for the RPt compounds [34].

To investigate whether there is an interaction between the 4f moments and spin fluctuations in the paramagnetic state we subtracted

$$(\rho(T) - \rho_0)_{\text{RCo}_2} - (\rho(T) - \rho_0)_{\text{LuCo}_2} \equiv \Delta\rho. \quad (10)$$

Under the assumption that $\rho_{ph}(T)$ for all these compounds is the same (they all have similar Debye temperatures [2]) $\Delta\rho$ enables us to show, at least qualitatively, whether there is an interaction between the spin fluctuations and 4f moments, i.e., whether above T_C ρ_{sf} in magnetic RCO_2 compounds is influenced by the 4f moments.

In figures 12–14 the temperature variation of $\Delta\rho$ in the temperature range from 4.2 K to 1000 K is presented. For all the magnetic RCO_2 compounds, $\Delta\rho(T)$ is nearly temperature independent at high temperatures as is expected for $\rho_{spd}(T)$; however, towards T_C , a pronounced increase is observed for PrCo_2 , NdCo_2 , ErCo_2 and HoCo_2 . In GdCo_2 ($T_C = 390$ K), TbCo_2 ($T_C = 233$ K) and SmCo_2 ($T_C = 203$ K) $\Delta\rho(T)$ remains constant when approaching T_C , while in DyCo_2 there is only a small effect. As can be seen from figure 14, TmCo_2 behaves exceptionally within the RCO_2 series, since its $\Delta\rho$ value drops down below about 180 K and exhibits a slight upturn in a very limited temperature region just above T_C . The increase of $\Delta\rho$ is obviously more pronounced if the magnetic order occurs in the temperature region where $d\rho/dT$ of the non-magnetic RCO_2 compounds has a maximum (i.e., around 50 K). Below T_C , $\Delta\rho$ sharply drops down with a minimum in some cases. This minimum is absent in the curves for PrCo_2 and TmCo_2 .

The minima and the negative values of $\Delta\rho$ below T_C are obviously caused by a suppression of the spin fluctuations and the gradual decrease of the spin disorder contribution

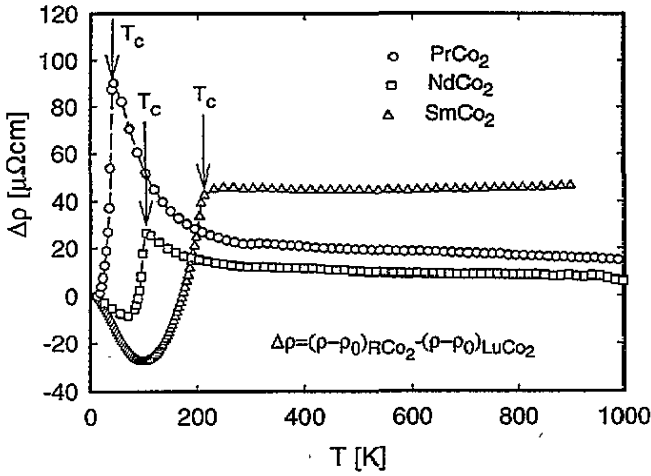


Figure 12. Temperature variation of $\Delta\rho$ for PrCo_2 , NdCo_2 and SmCo_2 .

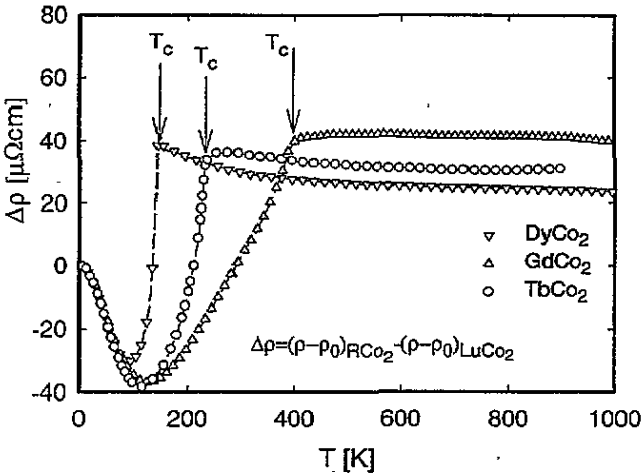


Figure 13. Temperature variation of $\Delta\rho$ for GdCo_2 , TbCo_2 and DyCo_2 .

due to the intersublattice $f-d$ molecular field. The behaviour of $\Delta\rho(T)$ just above T_C indicates a new source of scattering process and requires a detailed discussion.

We first consider the high-temperature limit of the absolute value of $\Delta\rho$ as taken at 800 K. Assuming that ρ_{spd} is independent of temperature at 800 K and taking both the phonon resistivity and ρ_{sf} of the magnetic compounds as equal to that of LuCo_2 we expect $\Delta\rho(800\text{ K})$ to be equal to ρ_{spd} , which should be proportional to the de Gennes factor [33]. In figure 15 the high-temperature values of $\Delta\rho$ for the heavy $R\text{Co}_2$ compounds are plotted as a function of the de Gennes factor. Within the experimental uncertainties the variation of $\Delta\rho$ is indeed linear. For comparison, ρ_{spd} of the RAI_2 and RPt series [21, 34] are also included in figure 15. In these latter series no paramagnetic spin fluctuation contribution in $\rho(T)$ was observed, and ρ_{spd} can correctly be determined by subtracting the total resistivity of the corresponding non-magnetic compound from that of the isostructural magnetic one [7]. The similar values of $\Delta\rho$ and ρ_{spd} for RAI_2 and RPt seem to confirm the validity of

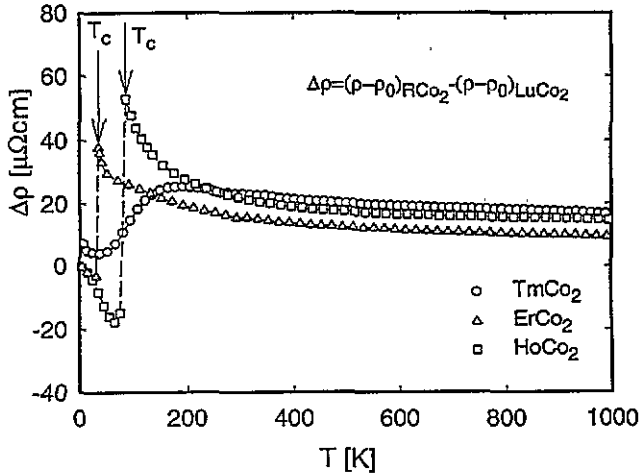


Figure 14. Temperature variation of $\Delta\rho$ for HoCo_2 , ErCo_2 and TmCo_2 .

the applied procedure. The values of $\Delta\rho(800\text{ K}) \approx \rho_{spd}$ are listed in table 1. Note that this proportionality to the de Gennes factor is not valid for the light-RE compounds.

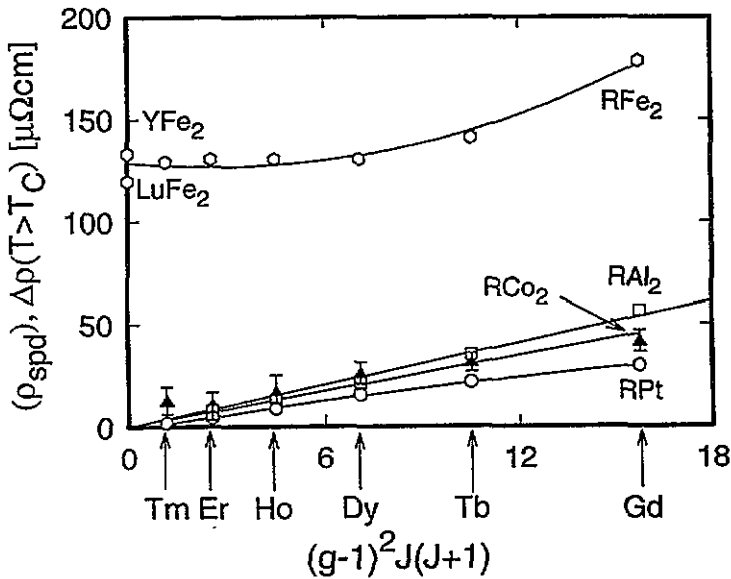


Figure 15. $\Delta\rho$ -values at 800 K for the heavy RCo_2 compounds as a function of the de Gennes factor. For comparison the spin disorder resistivities ρ_{spd} for RAl_2 , RFe_2 and RPt [34] are given.

Additionally, we have included in figure 15 $\rho_{mag}(800\text{ K})$ of the isostructural RFe_2 compounds [7]. The large values of ρ_{mag} even in the case of YFe_2 and LuFe_2 are caused by stable Fe 3d moments, which exist also in the paramagnetic state. Only a comparatively small increase towards GdFe_2 due to 4f-scattering processes is observable. We therefore conclude that the increase in $\Delta\rho$ versus T observed in some RCo_2 when approaching the Curie temperature is caused by the thermal variation of ρ_{sf} . Note that, as far as the upturn

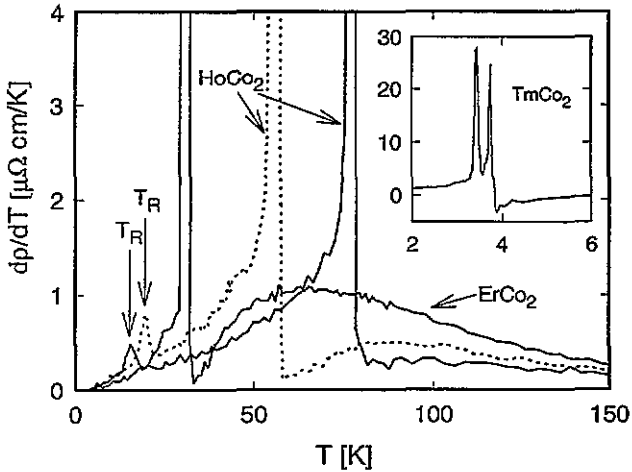


Figure 16. Temperature derivative $d\rho/dT$ for the heavy $R\text{Co}_2$ compounds ($R = \text{Ho}, \text{Er}$ and Tm). The dotted curve shows $d\rho/dT$ of HoCo_2 at 12 kbar external pressure. The spin reorientation temperature existing in HoCo_2 is indicated by T_R . The inset shows details of $d\rho/dT$ around $T_C (= 3.9 \text{ K})$ and the spin rearrangement transition at 3.4 K for TmCo_2 .

in $\Delta\rho$ is concerned, the anomaly is observable with any reference material, with only the size of the upturns at T_C being somewhat different.

The mechanism which is responsible for the increase in $\Delta\rho$ versus T is, in our opinion, the strengthening of correlations between the Co 3d electrons, which gives rise to increasing short-range magnetic order when the system approaches T_C from the paramagnetic temperature region. However, the observed strong increase in $\Delta\rho(T)$ cannot be explained by correlations between the 4f electrons only, i.e. without taking the spin fluctuation scattering into account. We assume that the correlations in the $R\text{Co}_2$ compounds are accompanied by an enhancement of the spin fluctuations within the d-electron subsystem beyond the intensity they show at the corresponding temperatures in non-magnetic $R\text{Co}_2$. The same subtraction procedure applied to the RPt [34] or RIn_3 [35] series, with magnetic 4f electrons only, gives much smaller anomalies above the ordering temperature. In the vicinity of T_C , the non-uniform fluctuating f-d exchange field provides an essential increase of the critical spin fluctuations in the itinerant d-electron subsystem. This in turn provides a rising and progressive strengthening of the scattering process of the conduction electrons on the enhanced critical spin fluctuations, which become suppressed below T_C . Further support for this argument is that the most pronounced increase of $\Delta\rho$ is observed in those compounds with Curie temperatures in the temperature region where the increase of ρ_{sf} itself is the strongest (compared with figure 2).

Based on the universality hypothesis, the influence of critical fluctuations on the resistivity was discussed in [36]. It has been shown that in the paramagnetic range near the Curie temperature the derivative $d\rho/dT$ changes its sign from negative to positive, which can hence lead to a visible increase in the $\rho(T)$ dependence. The change of the sign occurs when the correlation length becomes larger than the mean free path of the conduction electrons. A comprehensive description of this concept is given by Rossiter [37]. An attempt to analyse our $\Delta\rho$ versus T data using this model fails because the above theory of critical fluctuations is not applicable in the case of first-order phase transitions, which occur in most of the heavy $R\text{Co}_2$ compounds. Furthermore, the critical fluctuations, which are

considered to be responsible for the increase in $\Delta\rho$ above T_C , are of a different nature to those considered in that model, since in RCO_2 the 4f-moment fluctuations are accompanied by Co 3d-moment fluctuations, which dominate $\Delta\rho$ (and thus $d\Delta\rho/dT$) above T_C . However, below T_C there are no more Co 3d-spin fluctuations present, since they are now suppressed.

In order to improve the understanding of the influence of the critical fluctuations on the resistivity in the vicinity of the magnetic phase transition, we performed resistivity measurements under an external pressure. As already shown, pressure essentially decreases T_C in RCO_2 compounds. In particular, in the case of HoCo_2 one can follow the change of the $\rho(T)$ dependence due to the shift of T_C towards lower temperatures where the tendency to show an increase in $\rho(T)$ is more pronounced. In figure 16, $d\rho/dT$ is plotted for three compounds, HoCo_2 , ErCo_2 and TmCo_2 (in the inset). For HoCo_2 the variation of $d\rho/dT$ at an applied external pressure of 12 kbar is also shown. As can be seen, $d\rho/dT$ changes qualitatively under the pressure, since a maximum develops above T_C similarly as in $d\rho/dT$ of TmCo_2 and ErCo_2 .

In the above discussion we neglected the crystal field influence on the resistivity. Although there are no data available for the RCO_2 compounds, some general conclusions concerning the crystal field effect on the temperature dependence of $\Delta\rho(T)$ are possible. The crystal field splitting always leads to a negative curvature of $\rho_{3pd}(T)$ in the temperature range where the RE energy levels are thermally populated, therefore this effect cannot explain the observed increase in $\Delta\rho(T)$. The impact of crystal field splitting on $\Delta\rho(T)$ is obvious in case of TmCo_2 , the compound with the lowest Curie temperature (figure 14). The strong curvature above about 50 K is due to the crystal field level population with increasing temperature. However, even in TmCo_2 an upturn is observable in $\Delta\rho$ below about 10 K.

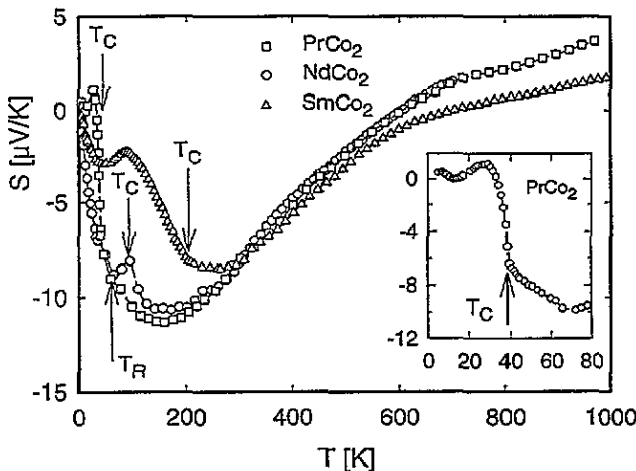


Figure 17. Temperature dependence of the thermopower of the light RCO_2 compounds ($R = \text{Pr}$, Nd and Sm). The inset shows details of S versus T around T_C for PrCo_2 .

3.2.2. Thermopower. Figures 17–19 show the temperature variation of the thermopower of the magnetic RCO_2 compounds. Comparing both the magnetic and non-magnetic RCO_2 compounds (figure 5) one can see that $S(T)$ at elevated temperatures is qualitatively very similar throughout the whole RCO_2 series. Above 150 K, the thermopower is negative

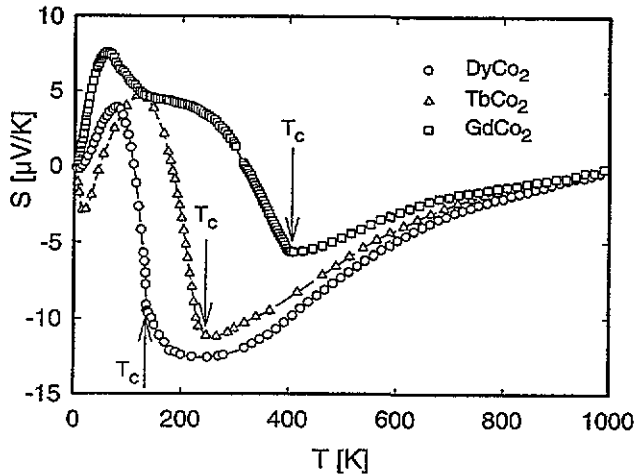


Figure 18. Temperature dependence of the thermopower of the heavy $R\text{Co}_2$ compounds ($R = \text{Gd}, \text{Tb}$ and Dy).

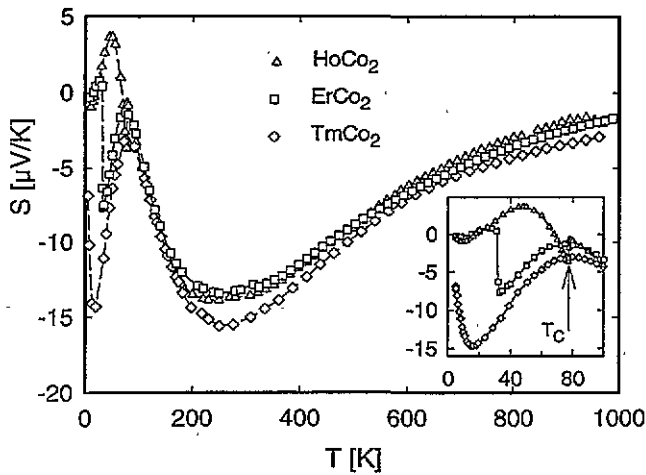


Figure 19. Temperature dependence of the thermopower of the heavy $R\text{Co}_2$ compounds ($R = \text{Ho}, \text{Er}$ and Tm). The inset shows details of S versus T in the vicinity of the magnetic ordering temperatures.

and shows a pronounced minimum with increasing temperature. In accordance with the discussion of the thermopower of YCo_2 , LuCo_2 and ScCo_2 (section 3.1.2) we suppose that the temperature variation of S at high temperatures is determined mainly by the density of states function and its derivatives around the Fermi level and is hardly influenced by various scattering mechanisms (in contrast to the resistivity). For example, the sign of $dN(\varepsilon)/d\varepsilon$ at ε_F determines the sign of $S(T)$, and the observed minima in S versus T can be understood if a local maximum in $N(\varepsilon)$ exists near ε_F [16]. As seen from figure 6, there is a linear relation between T_{min} and the γ value of the non-magnetic $R\text{Co}_2$ compounds. In the case of the magnetic $R\text{Co}_2$ compounds this relation is not observable. This is plausible since γ changes because of the band splitting below T_C . A close inspection of figures 5, 17 and 19

reveals that there is a linear relation between T_{min} and the lattice parameter among the $R\text{Co}_2$ series. This dependence is shown in figure 20. Due to high values of T_C , this minimum for GdCo_2 , SmCo_2 and TbCo_2 cannot be developed in the $S(T)$ dependences. The expected positions of T_{min} in these cases are marked by arrows in that figure.

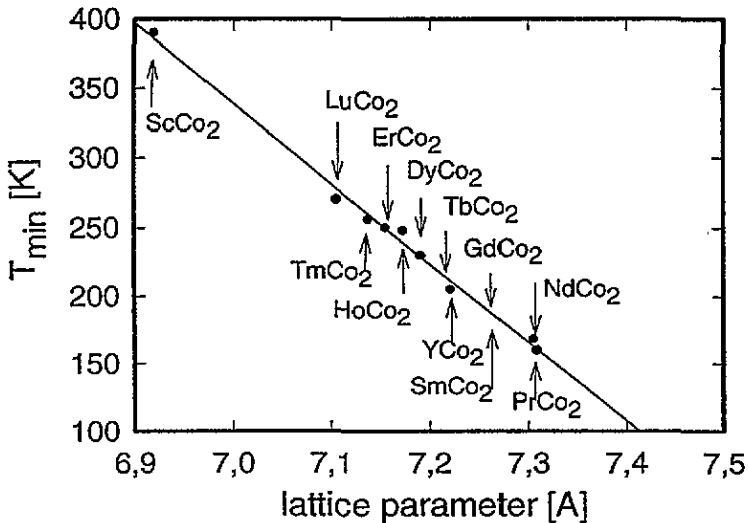


Figure 20. Relation between the position of the high-temperature minimum in the $S(T)$ dependences and the lattice parameter (at room temperature) of the $R\text{Co}_2$ compounds.

We relate this high-temperature minimum of $S(T)$ to a local maximum of $N(\epsilon)$ near the Fermi level. The existence of such a local maximum in YCo_2 has been confirmed by band structure calculations [5]. Because of the similar high-temperature behaviour of $S(T)$ in all the $R\text{Co}_2$ compounds it is certainly justified to assume that a local maximum near ϵ_F exists in all the $R\text{Co}_2$ compounds; however, the peak width varies with the lattice parameter.

4. Conclusion

The investigation of the transport properties of magnetic and non-magnetic $R\text{Co}_2$ compounds revealed that in these cubic Laves phases spin fluctuations influence essentially the temperature dependence of the transport properties. For the three non-magnetic $R\text{Co}_2$ compounds ($R = \text{Y}$, Lu and Sc) various features caused by the spin fluctuation scattering of the conduction electrons have been observed:

Electrical resistivity: A T^2 behaviour at low temperatures and a saturation tendency above, as predicted by the theory, has been confirmed. Beyond room temperature up to 1000 K, a decrease of the spin fluctuation resistivity has been found.

The spin disorder contribution ρ_{spd} to the total resistivity of the magnetic $R\text{Co}_2$ compounds was deduced using the high-temperature measurements. This contribution is proportional to the de Gennes factor as in the isostructural RAI_2 compounds.

Thermopower: The pronounced minimum observed in the temperature region where the resistivity follows the T^2 -behaviour refers to the influence of the spin fluctuations on the thermopower. Its origin has been brought in connection with a 'paramagnon-drag' effect.

The minimum in S versus T observed for YCo_2 , LuCo_2 and ScCo_2 at elevated temperatures has been explained by a special energy dependence of the density of states

function near the Fermi level (ε_F lies near the maximum of $N(\varepsilon)$). From the similarity of the $S(T)$ behaviour of all the RCo₂ compounds in the paramagnetic temperature region we concluded that $N(\varepsilon)$ around ε_F varies in a similar way in both the non-magnetic and magnetic RCo₂ compounds.

Thermal conductivity: At low temperatures, a $(1/T)$ -dependence of the spin fluctuation part of λ versus T has been identified for the non-magnetic RCo₂ compounds, as theoretically predicted for the spin fluctuation contribution. With increasing temperature, the spin fluctuation scattering causes a pronounced saturation, i.e. a nearly temperature independent experimental λ versus T behaviour. The thermal conductivity at elevated temperature is only half of the thermal conductivity of the isostructural non-spin fluctuation system YAl₂.

The transport properties of the magnetic RCo₂ compounds are strongly influenced by spin fluctuations above T_C ; the suppression of the spin fluctuations below T_C reduces considerably the total resistivity. In those cases where the magnetic transition is of first-order type, sharp discontinuities at T_C are observable in resistivity and thermopower. We may speak to some extent of a 'switching off' of the spin fluctuations at T_C .

Our experiments revealed that in magnetic RCo₂ there is an enhancement of the paramagnetic spin fluctuations near T_C beyond the intensity the non-magnetic RCo₂ compounds show at the corresponding temperatures. This enhancement increases when decreasing temperature towards T_C and is strongest in the compounds with T_C below about 200 K.

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