Gd substitutions in the TmCo$_2$ Laves phase: the onset of long-range magnetic order in the itinerant subsystem

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Abstract. We found that in TmCo$_2$ the molecular field does not exceed the critical value necessary to induce long-range magnetic order in the Co d-electron subsystem, which is in contrast to the other heavy RCo$_2$ compounds. Below $T_C = 3.8$ K a first-order magnetic phase transition at 3.4 K exists, which is due to a rearrangement of the Tm 4f magnetic moments. When substituting Tm by Gd long-range magnetic order appears in the Co d subsystem. The onset of the magnetic order in the d-electron subsystem can most clearly be seen from thermal expansion measurements. There is an increasing positive volume anomaly with increasing Gd content below T_C.

The estimated magnetostriction constant λ_{111} of TmCo$_2$ is -4.1×10^{-3}, in agreement with the single-ion model.

Pronounced discontinuities at T_C are characteristic for the transport properties (resistivity and thermopower) for TmCo$_2$ as well as for the pseudobinary Tm$_{1-x}$Gd$_x$Co$_2$ compounds. At elevated temperatures the physical properties of all these compounds are dominated by spin fluctuations.

1. Introduction

Among the intermetallic rare earth (RE or R) compounds with 3d transition metals the cubic Laves phase compounds RCo$_2$ are of particular interest. Due to the magnetic instability of the hybridized itinerant 3d–5d-electron subsystem (3d–4d in the case of YCo$_2$) and large magnetoelastic effects, these compounds exhibit a number of characteristic properties which make them appropriate for checking various physical theories. In contrast to the isostructural RNi$_2$ and RFe$_2$ compounds, in which the d-electron subsystem is either non-magnetic (RNi$_2$) or bears a stable magnetic moment (RFe$_2$), the RCo$_2$ compounds exhibit to some extent an intermediate behaviour [1–3]. Those RCo$_2$ compounds with non-magnetic Y and Lu are exchange enhanced Pauli paramagnets and undergo a metamagnetic transition, i.e. a field-induced magnetic phase transition from the paramagnetic to the ferromagnetic state under an external magnetic field exceeding a certain critical value H_C. This critical field of the metamagnetic transition was found to be 69 and 75 T for YCo$_2$ and LuCo$_2$, respectively [4]. In the RCo$_2$ compounds with magnetic RE ions the molecular field exceeds the critical field

H_C necessary to induce a ferromagnetic order in the d-electron subsystem. The induced d moment per Co atom (about $1\mu_B$) is dependent on the RE ion within the heavy RCo$_2$ series [3], [12]. Neutron diffraction studies revealed a simple collinear ferrimagnetic structure in the heavy RCo$_2$ compounds [5–8].

Most of the magnetic and transport properties of the RCo$_2$ compounds are substantially influenced by the onset of the long-range magnetic order in the d-electron subsystem. The first-order magnetic phase transition in DyCo$_2$, HoCo$_2$ and ErCo$_2$ is accompanied by pronounced anomalies in the temperature dependence of the magnetization, the thermal expansion and the transport properties at the Curie temperature. In particular, large discontinuities observed in the temperature variation of the electrical resistivity of the RCo$_2$ compounds were attributed to the suppression of spin fluctuations in the itinerant subsystem due to the magnetic order below T_C [9]. The large magnetovolume effect at T_c ($\Delta V / V > 1 \times 10^{-3}$) observed in the RCo$_2$ compounds also originates from the onset of long-range magnetic order in the itinerant d-electron subsystem, while the huge anisotropic magnetostriction of the order of 10^{-3} is mainly determined by the crystal-field interaction of the localized 4f electrons of the magnetic RE ions [10–12].

Because of its low ordering temperature TmCo$_2$ has been much less investigated compared to the other RCo$_2$ compounds. In the literature there are some indications of a first-order magnetic phase transition in TmCo$_2$; however, the given temperatures range from 2 to 7 K [13]. The estimated Co moment, $0.8\mu_B$/FU at 4.2 K [5], is smaller than that for the other heavy RCo$_2$ compounds. Recently the intersublattice molecular-field coefficient of the Tm–Co exchange interaction, $n_{TmCo} = (13.5 \pm 1)$ T/(μ_B FU), was determined from the observation of non-collinear magnetic structures induced by an external magnetic field in the Lu$_{1-y}$Tm$_y$(Co$_{0.88}$Al$_{0.12}$)$_2$ system [14]. An estimation of the molecular field acting on the d subsystem in TmCo$_2$, $H_{fd}^{(Co)}$, gives a value of about 60 T. This value is very close to the critical field of the metamagnetic transition H_C [4]. Therefore for TmCo$_2$ one can expect a magnetic behaviour different from those of the other heavy RCo$_2$ compounds.

The purpose of the present work was to clarify the magnetic behaviour of the d-electron subsystem in TmCo$_2$ and its evolution in the Tm$_{1-x}$Gd$_x$Co$_2$ pseudobinary system, in which the Gd substitutions provide a regular increase of the molecular field. Gadolinium has been chosen as a diluent to avoid any additional crystal-field influence on the physical properties.

2. Experimental details

Polycrystalline samples of Tm$_{1-x}$Gd$_x$Co$_2$ ($x = 0$; 0.05; 0.1; 0.15 and 0.2) have been prepared under a protective argon atmosphere by induction melting of the constituents in a water cooled copper boat. Subsequently the samples were homogenized at 800 °C for one week. An off stoichoimetry of 1:1.92 was chosen to ensure foreign phase free ingots. The phase purity of all the samples had been checked by x-ray diffraction. Within the resolution of this analysis, the foreign phases which might exist in the samples are less than 2%. The AC-susceptibility measurements were carried out by using a conventional compensated AC susceptometer in the temperature range from 2 to 100 K. A Nernst calorimeter was used for the specific heat measurements in the range from 1.5 to 50 K. Electrical resistivity data were obtained in the range from 1.5 to 300 K by means of a conventional four-probe technique. A differential method was used for the thermopower measurement from 4 to 300 K with lead as the reference material. The thermal expansion and lattice distortion were measured in the temperature range from 4 to 300 K using an x-ray diffractometer with a helium flow cryostat mounted instead of the conventional sample holder. The low-temperature

(2.5–15 K) thermal expansion of $TmCo_2$ was measured in various magnetic fields in a capacitance dilatometer with the field applied parallel to the measurement direction.
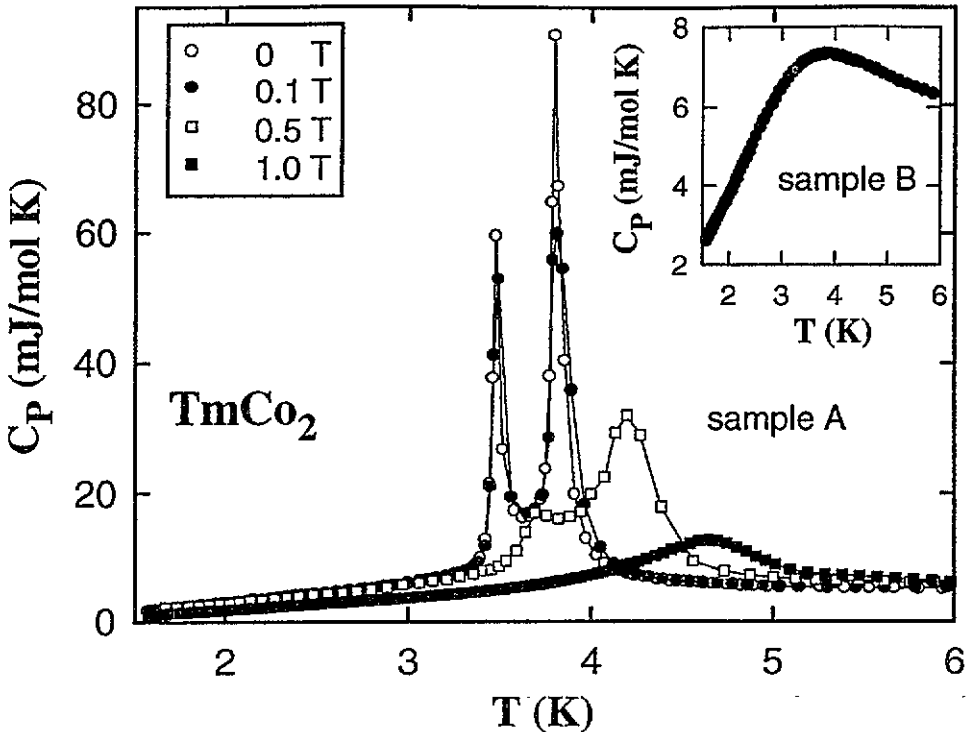

Figure 1. The temperature dependence of the specific heat of $TmCo_2$ (sample A) with two magnetic phase transitions at low magnetic fields. The inset shows the data for sample B.

3. Experimental results

3.1. TmCo₂

In figure 1 the temperature variation of the specific heat c_p of $TmCo_2$ for various magnetic fields is shown. Two samples, prepared using the same technique (denoted below as A and B), were measured. The $c_p(T)$ curve of sample A at zero field shows two phase transitions at 3.8 K and 3.4 K. Both transitions are characterized by narrow symmetric peaks typical for a first-order phase transition. While the high-temperature peak could be interpreted as the Curie point T_C, the low-lying peak indicates a second phase transition, which was not mentioned in the previous literature [5], [13]. The magnetic field broadens both transitions and shifts them towards higher temperatures, the low-temperature transition being not observable in fields higher than 1 T. In sample B, the specific heat exhibits only one broad maximum at 3.8 K, which can be identified as the Curie point. Note that the Curie temperature found for $TmCo_2$ is considerably lower than the 7 K reported in [5]. We attribute the different behaviour of the samples A and B to small differences in their stoichiometry and to the influence of inhomogeneities in sample B.

Figure 2 shows the temperature dependence of the electrical resistivity ρ of $TmCo_2$ (sample A). For comparison the ρ against T curve of the isostructural non-magnetic $LuCo_2$
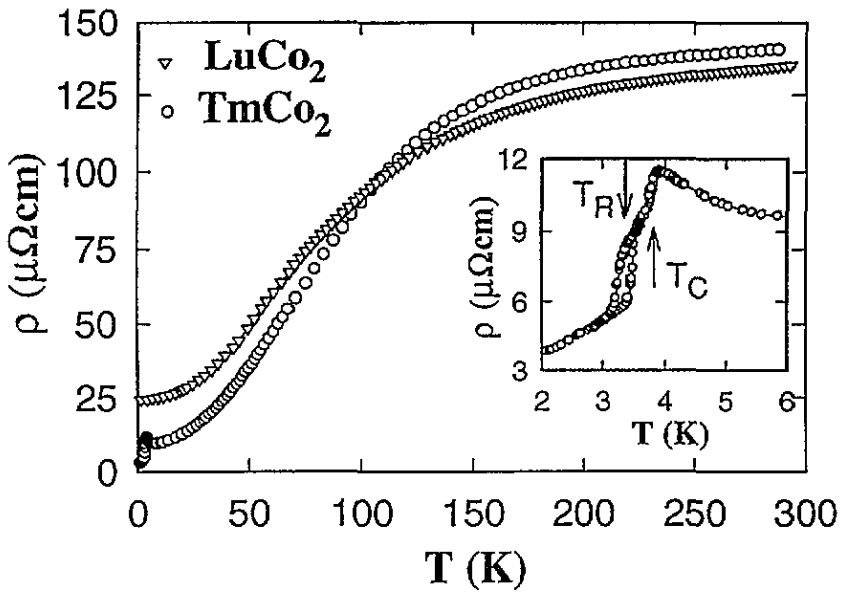
Figure 2. The temperature dependence of the electrical resistivity of TmCo$_2$ (sample A) and LuCo$_2$. The inset shows the low-temperature behaviour of $\rho(T)$ for TmCo$_2$ (arrows indicate the transition temperatures taken from the $c_p(T)$ data (figure 1)).

compound is included in that figure. Both curves are very similar in their temperature variation, in particular, both show the same saturation tendency above about 150 K. The $\rho(T)$ curve of TmCo$_2$, however, exhibits a discontinuity below 4 K. A closer inspection reveals that it is a two-step transition (see inset in figure 2). The higher one corresponds to T_C as observed in the specific heat. Towards lower temperatures the steplike change in ρ against T, with a narrow hysteresis, indicates the second transition. Important information on the magnetic state of TmCo$_2$ can be obtained by studying the thermal expansion. In figure 3 the temperature dependence of $\Delta l/l$ for TmCo$_2$ (sample A) is presented. Both transitions are accompanied by a volume contraction with decreasing temperature. However most of the shrinking appears at the Curie temperature at 3.8 K. The whole volume change $\Delta V/V = 3\Delta l/l$ is about -6.5×10^{-4}. This observed $\Delta l/l$ against T dependence is completely different from those of the other RCo$_2$ compounds with magnetic RE, in which a large positive volume expansion exceeding 1×10^{-3} arises due to long-range magnetic order in the itinerant Co d subsystem. The effect of an external field is similar to that observed in the specific heat. The low-temperature transition seems to disappear at about 1 T while that identified as the Curie point becomes considerably broader. It is important to underline the absence of any positive volume effect with decreasing temperature, which would indicate an onset of d magnetism in TmCo$_2$ under an external field. The inset in figure 3 shows the thermal expansion of sample B. $\Delta l/l$ shows a volume contraction roughly of the same order of magnitude as that of sample A. However, in sample B the magnetic transition is less sharp even at zero field.

The temperature-dependent AC susceptibility of TmCo$_2$ (sample A) is shown in figure 4. Only one broad and very asymmetric maximum in the real part $\chi'_{AC}(T)$ is observed around 3.6 K. Below the maximum, the susceptibility sharply drops down, which is characteristic of a first-order phase transition. We point out that in this region the dissipative part of the susceptibility $\chi''_{AC}(T)$ shows a maximum. The $\chi'_{AC}(T)$ dependence of sample B is shown in
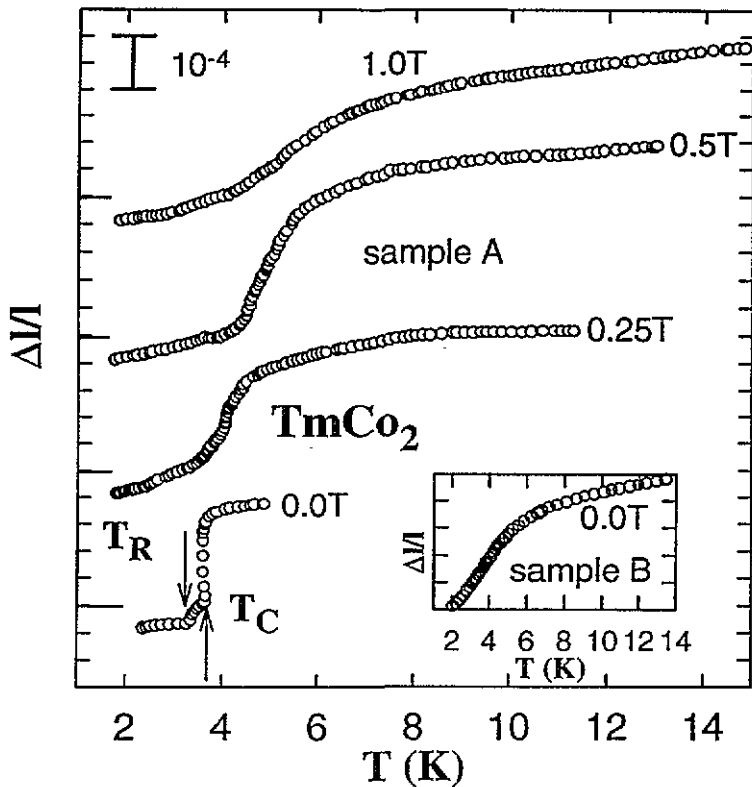
Figure 3. The thermal expansion $\Delta l/l$ of $TmCo_2$ (sample A) at low temperatures measured at different external fields (arrows indicate the transition temperatures taken from the $c_p(T)$ data). The inset shows the zero-field dependence for sample B. For clarity, the $\Delta l/l$ curves for different fields are correspondingly shifted. The $\Delta l/l$ scales are the same in figure and inset.

the inset in figure 4. The comparison of the susceptibility of sample B with that of sample A reveals that sample B does not show the discontinuous decrease (see the inset in figure 4), but a further increase with decreasing temperature. Furthermore there is a hump around about 5 K which is not visible in sample A. Because of this susceptibility behaviour of sample B we assume that it is contaminated by a small amount of Tm_4Co_3, the Tm-richest phase in the Tm–Co phase diagram which is nearest to $TmCo_2$. Tm_4Co_3 has a magnetic transition at about 5 K.

3.2. $Tm_{1-x}Gd_xCo_2$

3.2.1. Specific heat. The temperature dependence of the specific heat of the $Tm_{1-x}Gd_xCo_2$ compounds is shown in figure 5. The Gd substitution changes drastically the c_p against T dependence of $TmCo_2$. The two-peak structure observed for pure $TmCo_2$ (see sample A in figure 1) is changed into a broad hump around 7 K for $Tm_{0.95}Gd_{0.05}Co_2$. With increasing x only one peak is observable, its position shifted towards higher temperatures. Under an external magnetic field the transition occurs at higher temperatures. As an example, the results for $Tm_{0.9}Gd_{0.1}Co_2$ at 0 and 1.0 T are compared in the inset of figure 5.
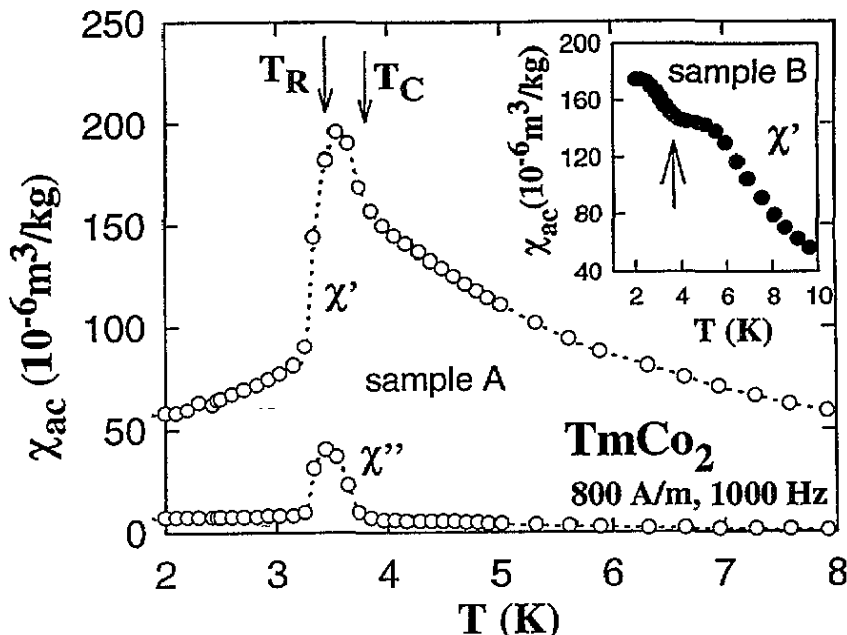
Figure 4. The real (χ'_{AC}) and imaginary (χ''_{AC}) parts of the AC susceptibility of TmCo$_2$ (sample A) as a function of temperature (arrows indicate the transition temperatures taken from the $c_p(T)$ data). The inset shows the $\chi'_{AC}(T)$ dependence for sample B (the Curie temperature taken from the $c_p(T)$ dependence is indicated by an arrow).

3.2.2. Electrical resistivity. In figure 6 the temperature dependence of the electrical resistivity ρ for $x \geqslant 0.05$ is shown. For comparison the $\rho(T)$ curve of LuCo$_2$ is also presented. We note that the shallow minimum above T_C observed in TmCo$_2$ is much more pronounced for $x = 0.05$ and $x = 0.1$, but it disappears on further increasing x. The ρ against T curves for compounds with $x \geqslant 0.1$ are characterized by steplike discontinuities at T_C similar to those observed in the other heavy RCo$_2$ compounds [9].

3.2.3. Thermopower. The temperature variation of the thermopower (S) for different Gd concentrations is given in figure 7. Again the $S(T)$ data for LuCo$_2$ are included. Above about 100 K, the S against T dependence is similar for all these compounds irrespective of whether local 4f moments at the RE sites exist or not (as in LuCo$_2$). The pronounced minimum around 20 K observed in S against T for TmCo$_2$ diminishes progressively with increasing x. Simultaneously a kink (see inset) appears, indicating the onset of magnetic order for $x = 0.10$, 0.15 and 0.2. The arrows shown in the inset indicate the Curie temperatures for these x values.

3.2.4. Thermal expansion and anisotropic magnetostriction. In figure 8 the temperature dependence of the lattice parameter of the Tm$_{1-x}$Gd$_x$Co$_2$ compounds and LuCo$_2$ (normalized to 180 K) is given. Down to 4.2 K no upturn in the lattice parameter is observed for TmCo$_2$ and Tm$_{0.95}$Gd$_{0.05}$Co$_2$ or in paramagnetic LuCo$_2$. With further Gd substitution a sharp increase in the unit cell volume appears below T_C, as in other heavy RCo$_2$ compounds [12]. Similar to RCo$_2$, in which the magnetovolume effect depends on the type of the RE ion, in the Tm$_{1-x}$Gd$_x$Co$_2$ system the magnetovolume effect increases
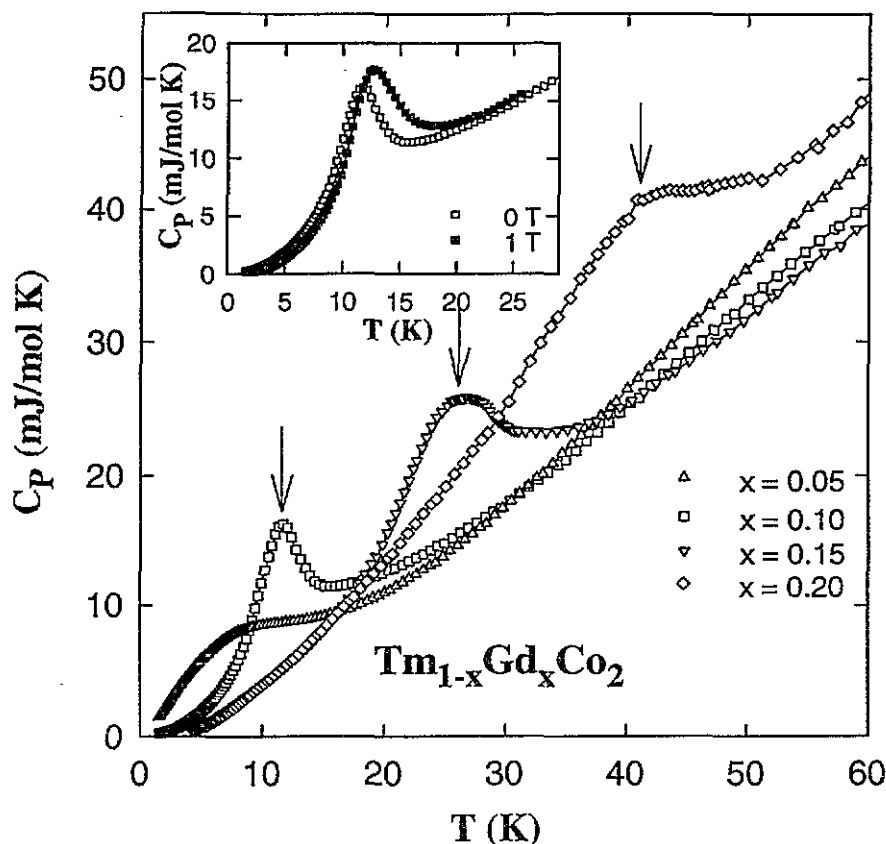
Figure 5. The temperature variation of the specific heat of the $Tm_{1-x}Gd_xCo_2$ compounds (arrows indicate the position of T_C). In the inset the data for $x = 0.1$ in zero magnetic field and in a field of 1 T are shown.

considerably with x.

The low-temperature x-ray diffraction measurements reveal that below T_C a rhombohedral distortion of the cubic Laves phase unit cell appears in all substituted compounds except $x = 0.05$. The rhombohedral distortion can be described using the parameter $\Delta = (\delta d_{111})/d_{111}$, where d_{111} is the interplanar spacing of the (111) planes. In figure 9 the values of $(2/3)\Delta$ for the $Tm_{1-x}Gd_xCo_2$ compounds are plotted as a function of temperature. The distortion decreases monotonically with increasing temperature, its sign being negative for all the compounds studied.

4. Discussion

From the above results it follows that the behaviour of $TmCo_2$ in the ordered state differs substantially from that of the other heavy RCo_2 compounds. The narrow and symmetric peak in $c_p(T)$ as well as the sharp discontinuity in the volume at the high-temperature phase transition point (see figures 1 and 3) observed in $TmCo_2$ can be interpreted as a consequence of a first-order phase transition at T_C. In $TmCo_2$ this first-order transition cannot be attributed to the itinerant-electron metamagnetism (as in $ErCo_2$, $HoCo_2$ and $DyCo_2$), since the condition for the metamagnetic transition of the d-electron system is
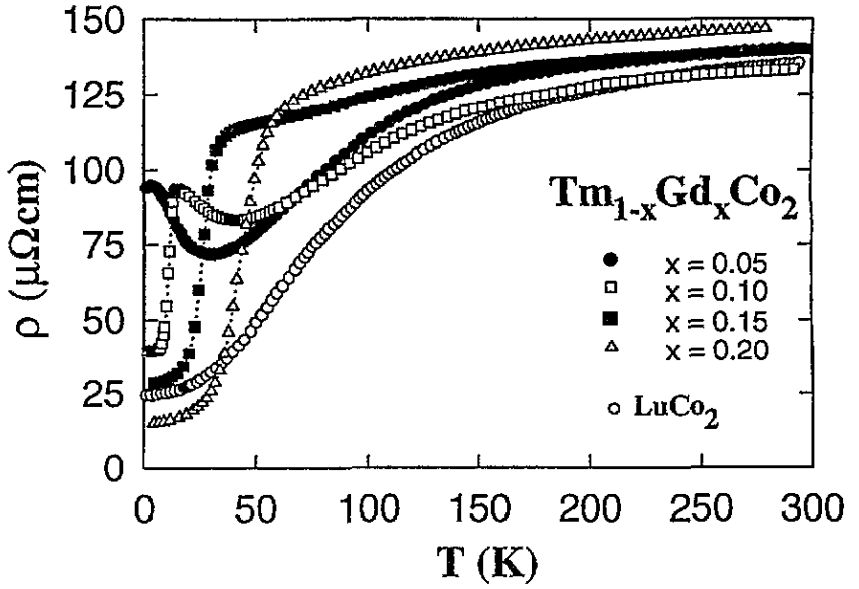
Figure 6. The temperature dependence of the electrical resistivity of the $Tm_{1-x}Gd_xCo_2$ compounds. Data for the isostuctural non-magnetic $LuCo_2$ compound are given for comparison.
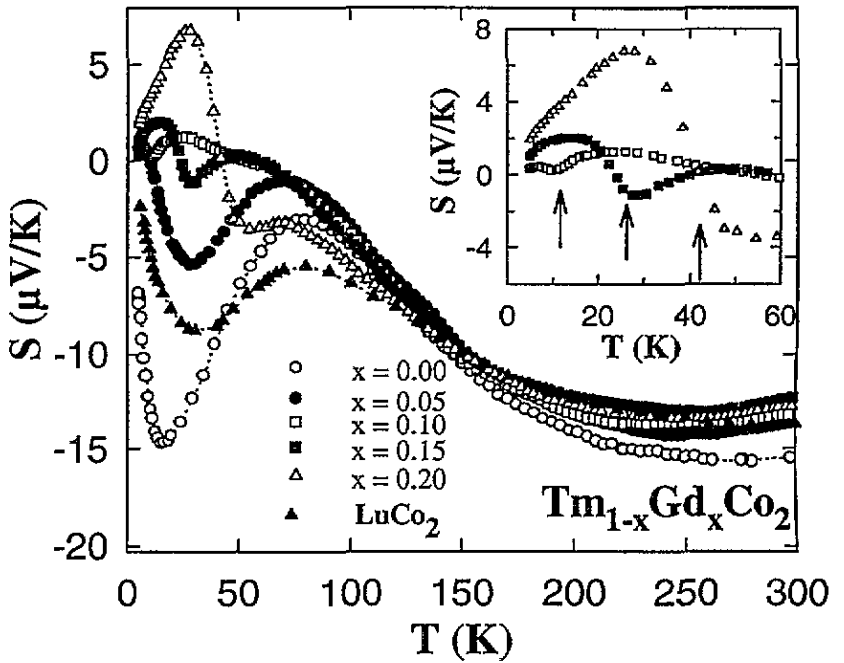

Figure 7. The temperature dependence of the thermopower of the $Tm_{1-x}Gd_xCo_2$ compounds. Data for the isostructural non-magnetic $LuCo_2$ compound are given for comparison. The inset shows the low-temperature range for the compounds with $x = 0.10$, 0.15 and 0.20 (arrows indicate the Curie temperatures taken from the $c_p(T)$ data (figure 5)).

not fulfilled. This transition would be accompanied by a large positive volume anomaly
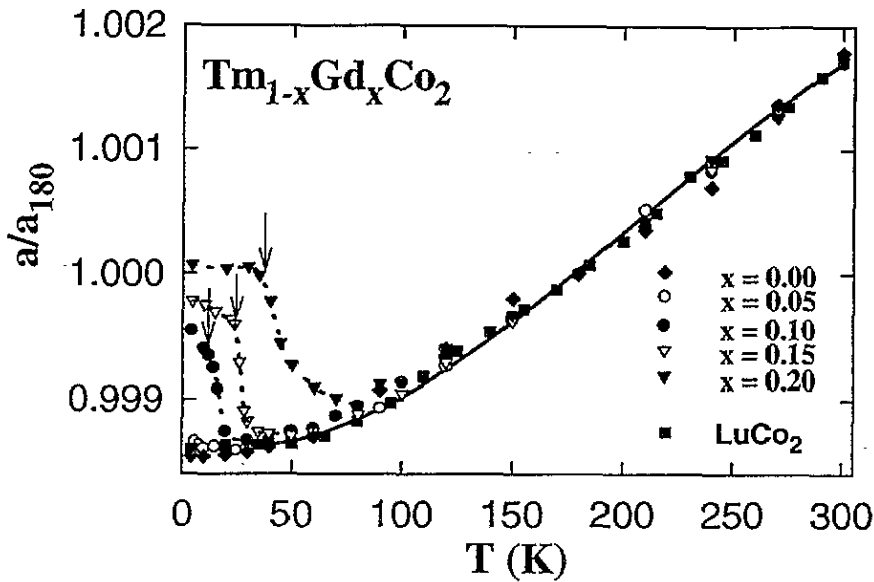
Figure 8. The temperature dependence of the lattice parameter of the $Tm_{1-x}Gd_xCo_2$ compounds normalized to 180 K. In the rhombohedrally distorted range (below T_C) the values of $\sqrt[3]{V/V(180\ K)}$ have been used. The arrows indicate the Curie temperatures taken from the $c_p(T)$ data (figure 5).
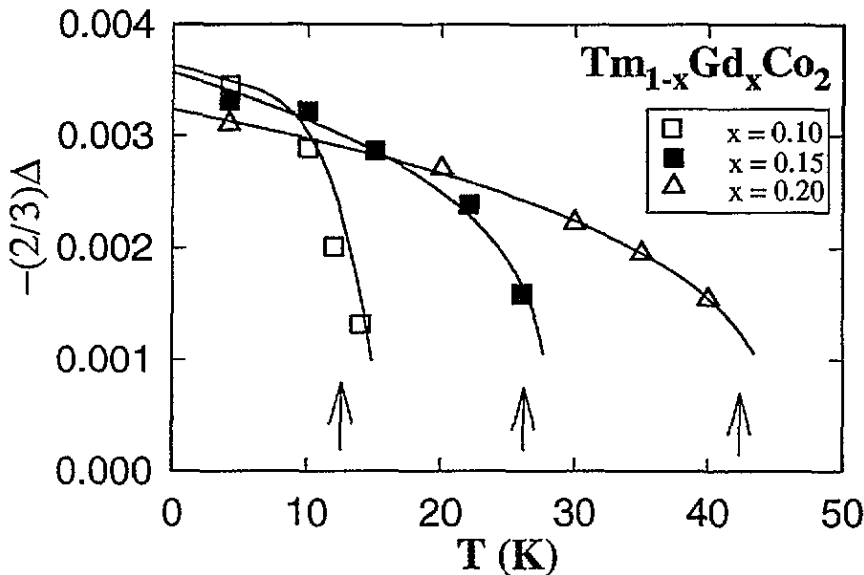

Figure 9. The rhombohedral distortion $-(2/3)\Delta$ for the $Tm_{1-x}Gd_xCo_2$ compounds. The lines are drawn as a guide for the eyes. The arrows indicate the Curie temperatures taken from the $c_p(T)$ data (figure 5).

(magnetovolume effect) larger than 1×10^{-3}. Its origin is intimately connected with a gain of energy due to a decrease of the kinetic energy of the d electrons through the lattice expansion [15]. In the Gd-substituted $Tm_{1-x}Gd_xCo_2$ compounds the condition for the metamagnetic

transition is fulfilled (at least for $x \geqslant 0.1$) and the Co (or d) magnetic moment is connected with the observed value of the volume anomaly ω_s by the simple expression [15]

$$\omega_s = kCM_{Co}^2 \tag{1}$$

where kC is the magnetoelastic coupling coefficient, M_{Co} denotes the d magnetic moment per Co atom and $\omega_s = (V_m - V_p)/V_p$, where V_m and V_p are the volumes in the magnetic and non-magnetic state, respectively. The absence of a positive magnetovolume effect in TmCo$_2$ has to be considered as convincing proof that, at least down to 2.5 K, there is no long-range magnetic order in the itinerant Co d-electron subsystem. This result is in contradiction to the results in [5] where the Co d-electron subsystem was found to be magnetically ordered in TmCo$_2$.

The large spontaneous positive magnetovolume effect observed in the Tm$_{1-x}$Gd$_x$Co$_2$ compounds with $x \geqslant 0.1$ shows that Gd substitutions in TmCo$_2$ give rise to long-range magnetic order in the itinerant-d-electron subsystem. The sample with $x = 0.05$ is an exception: the measurements performed on this sample do not fit into the general tendency observed for the other Gd concentrations. As seen from figure 10, the magnetovolume effect increases with increasing x. The values of ω_s were obtained by using $a(T)$ of LuCo$_2$ as a non-magnetic reference material. Assuming that the magnetovolume coupling coefficient kC in (1) is equal for all the heavy RCo$_2$ compounds (8.14×10^{-3} $(\mu_B^2/\text{Co})^{-1}$ [12]), we are able to determine the concentration dependence of the d moment, M_{Co}. These results are given in the inset in figure 10. As can be seen, there is a smooth increase of M_{Co} with increasing Gd concentration.
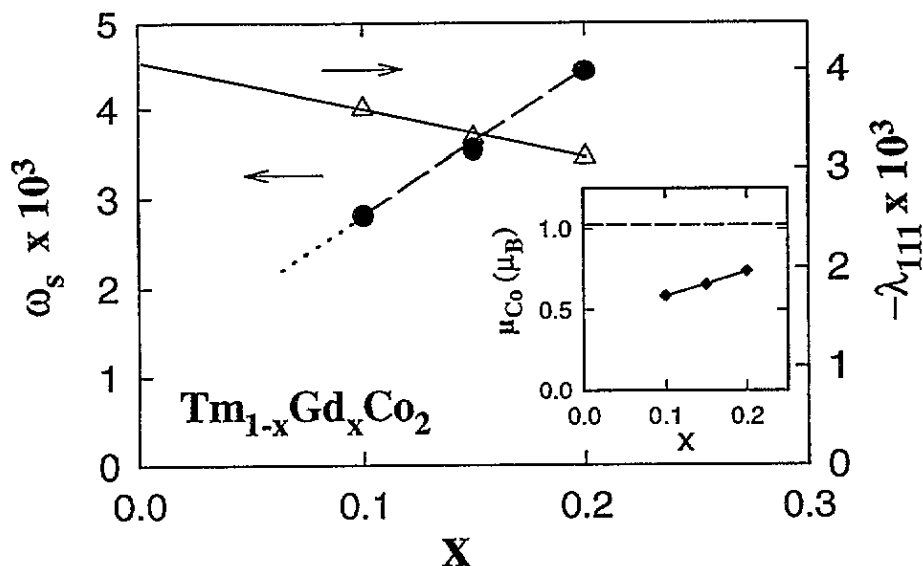

Figure 10. The magnetostriction constant λ_{111} (open triangles) and magnetovolume effect ω_s (full circles) of Tm$_{1-x}$Gd$_x$Co$_2$ compounds as a function of the Gd concentration at 4.2 K. The inset shows the concentration variation of the d magnetic moment (per Co atom) calculated by using (1). The dotted horizontal line represents the value of M_{Co} of GdCo$_2$.

In the mean-field approximation, the magnetic field acting on the Co ions is given by

$$H_{fd}^{(Co)} = (1-x)n_{TmCo}\bar{M}_{Tm} + xn_{GdCo}M_{Gd} + n_{CoCo}M_{Co}. \tag{2}$$
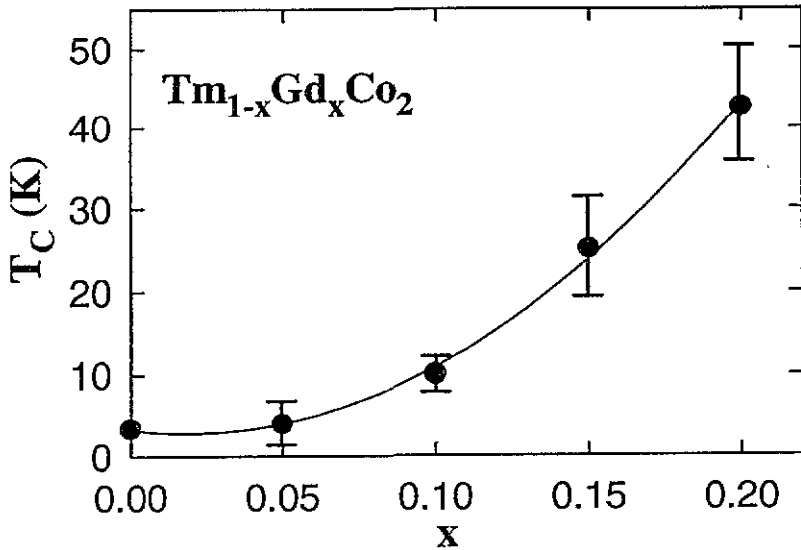
Figure 11. The Curie temperature of the $Tm_{1-x}Gd_xCo_2$ compounds as a function of the Gd concentration. The line is drawn as a guide for the eyes.

Here, n and M with indices denote the corresponding molecular field coefficients and magnetizations, respectively. Since n_{GdCo} is larger than n_{TmCo}, $H_{fd}^{(Co)}$ increases with increasing Gd concentration, thus favouring the onset of long-range magnetic order in the itinerant subsystem at $H_{fd}^{(Co)} = H_C$ as well as the increase of M_{Co} in the ordered state.

The concentration dependence of the Curie temperature of the $Tm_{1-x}Gd_xCo_2$ system as determined from $c_p(T)$ and $\rho(T)$ is depicted in figure 11. The strong non-linear increase of T_C is obviously caused by the (f–d) exchange interaction which increases with increasing Gd content. However, the substitution of Tm by Gd causes a non-uniformity of the molecular field, thus smearing the onset of the magnetic transition. This broadening can most clearly be seen in the specific heat given in figure 5. Except the sample with $x = 0.05$ the sharpness of the transition decreases with increasing x. In the substituted compounds with ordered itinerant Co d subsystem ($x \geqslant 0.1$) the magnetic transition should be of first-order type, due to the itinerant-electron metamagnetism [3]. From our experiments it is difficult to decide whether they are of first- or second-order type. The vertical error bars in figure 11 show the uncertainty in determining T_C due to the broadening of the phase transitions.

One possible mechanism of the second transition at 3.4 K in $TmCo_2$ could be a strong quadrupole–quadrupole interaction [16]. We assume that this interaction can give rise to a rearrangement of the magnetic structure in the magnetically ordered state as well as to the first-order phase transition at T_C. Unfortunately, there are no data available on the quadrupole interaction parameters in $TmCo_2$ with which to perform reasonable estimates. In $TmCo_2$ the quadrupole interaction can be enhanced due to a large contribution of the d-electron subsystem to the indirect f–(s, p, d)–f exchange interaction. Further detailed studies are necessary to clarify the origin of the first-order phase transitions in $TmCo_2$. The anisotropic 4f-electron distribution of the Tm^{3+} ions is also responsible for the spontaneous lattice distortion observed in the $Tm_{1-x}Gd_xCo_2$ compounds in the ordered state (due to the alignment of the 4f shells in the crystal field: single-ion mechanism). The lattice distortion is related to the anisotropic magnetostriction [11]. For a single-domain cubic crystal the anisotropic magnetostriction in any direction (given by the direction cosines β) is given by

the well known expression

$$\lambda_{anis} = \frac{3}{2}\lambda_{100} \sum_i (\alpha_i^2 \beta_i^2 - 1/3) + 3\lambda_{111} \sum_{i<j} \alpha_i \alpha_j \beta_i \beta_j \tag{3}$$

where α are the direction cosines of the magnetization ($i, j = x, y, z$). It follows from (3) that a rhombohedral distortion occurs if the magnetization direction is the [111] axis. Then the spontaneous magnetostriction is determined by the expression

$$\lambda_{111} = (2/3)\Delta \tag{4}$$

where Δ is given by $\Delta = (\delta d_{111})/d_{111}$ (see above). Because in the Gd-substituted compounds the Curie temperature is substantially higher than 4 K, one can assume that especially the samples with $x \geqslant 0.1$ are close to saturation at 4 K. Therefore the data extrapolated to $x = 0$ can be considered as a good approximation for TmCo$_2$ in the ground state. The magnetostriction constants λ_{111} at 4 K of the Tm$_{1-x}$Gd$_x$Co$_2$ compounds as a function of the Gd content are shown in figure 10. According to [11] there is no Co contribution to λ_{111} in the heavy RCo$_2$ compounds. Since Gd^{3+} is an S state ion, the anisotropic magnetostriction constant of this system is entirely determined by the Tm^{3+} ions and, in the scope of the single-ion model, it should be a linear function of the Tm concentration. The linear extrapolation (see figure 10) gives a value of $\lambda_{111} = -4.1 \times 10^{-3}$ for TmCo$_2$, which is in agreement with the single-ion theory [11] with respect to both its sign and value.

The transport phenomena (resistivity and thermopower) give very instructive informations on the spin-fluctuation dynamics in the Co d-electron subsystem. The influence of the spin fluctuations on the transport phenomena is very strong because the characteristic time of the fluctuating d moments is of the same order of magnitude as the time window of the transport phenomena (where the conduction electrons serve as probes). Recently it was shown [17] that the pronounced saturation in $\rho(T)$ observed for the non-magnetic RCo$_2$ (R = Sc, Y, Lu) compounds, as well as the T^2 behaviour at low temperatures, can be well explained by spin-fluctuation scattering. In the RCo$_2$ Laves phases with magnetic RE, the magnetic contribution to the resistivity is assumed to consist of two spin-dependent parts at temperatures well above T_C: the first being due to scattering processes of the conduction electrons on the localized 4f moments, and the second due to the scattering on the Co 3d-electron spin fluctuations (as in LuCo$_2$). The large discontinuity in ρ against T at T_C, as observed in ErCo$_2$, HoCo$_2$ and DyCo$_2$ [9], is caused by the suppression of these spin fluctuations due to the onset of the long-range magnetic order. From this point of view and in accordance with the mentioned reasons, one has to expect a large discontinuity at $T = T_C$ in $\rho(T)$ for the Gd-substituted compounds. Indeed, as shown in figure 6, there are quite sharp increases at T_C for $0.1 \leqslant x \leqslant 0.2$; however, they are less sharp than those of the pure RCo$_2$ (R = Er, Ho, Dy) compounds. Again the sample with $x = 0.05$ is an exception, since we do not observe any discontinuity in ρ against T. Concerning the other Gd contents: when the magnetic order takes place at low temperatures, the thermal spin fluctuations are not yet fully developed, therefore the step in ρ at T_C increases with increasing x (higher T_C). Recent investigations revealed that the contribution of the thermally induced spin fluctuations becomes approximately the same for all RCo$_2$ and substituted R$_{1-x}$Y$_x$Co$_2$ compounds only above 200 K [18, 21].

Another peculiarity in the $\rho(T)$ dependence of the Tm$_{1-x}$Gd$_x$Co$_2$ compounds is the minimum above T_C observed in TmCo$_2$ and the low-substituted compounds with $x = 0.05$ and $x = 0.1$ (see figure 6). It seems that in the paramagnetic region, when approaching T_C, short-range correlations between the 4f moments enhance the spin fluctuations in the

d-electron subsystem (via (f–d) interaction). This enhancement decreases with increasing temperature and, together with the increasing thermally induced spin fluctuations, they may give rise to the minimum in ρ against T above T_C. This effect is more pronounced in the compounds with low x because the thermally induced spin fluctuations are weaker at lower T_C.

For the discussion of the temperature dependence of the thermopower it is necessary to consider again the behaviour of LuCo$_2$ (see figure 7). The S against T curve of this spin-fluctuation system is characterized by a minimum in the low-temperature region around 30 K and a second broader one near room temperature. As can be seen from figure 7, the general slope of the S against T curves above about 100 K for all the investigated compounds is similar to that of LuCo$_2$. Although no S against T data above room temperature are available for these compounds, there are reasons to assume that the $S(T)$ curves have a broad minimum as observed for all the heavy RCo$_2$ compounds [22]. A qualitative analysis of the $S(T)$ data of YCo$_2$ from 100 K up to 1000 K [23] shows that mainly the density of states features of the d subsystem determine the sign and the curvature of S against T in the high-temperature region. Several reasons, such as phonon drag or Nielsen–Taylor effects, have been discussed in the literature to explain the appearance of a minimum in the thermopower at low temperatures (both can yield a pronounced non-linear behaviour at low temperatures) [19, 20]. In spin-fluctuation systems such as the $Tm_{1-x}Gd_xCo_2$ compounds, however, we assume that for $x = 0$ and $x = 0.05$ as well as for LuCo$_2$ this minimum is intimately related to the existence of spin fluctuations. Note that a very deep minimum exists in nearly all the other known spin-fluctuation systems, e.g., UAl$_2$ [24, 9]. The thermopower minimum is much more pronounced in TmCo$_2$ compared to LuCo$_2$ because of the enhancement of the spin fluctuations just above T_C in TmCo$_2$ (see the resistivity discussion above). The enhanced spin fluctuations are suppressed below T_C, therefore the observed minimum vanishes for higher Gd concentrations (higher T_C).

5. Conclusion

The results of the work can be summarized as follows.

(i) In contrast to the other RCo$_2$ compounds, in TmCo$_2$ there is no long-range magnetic ordering in the itinerant Co d subsystem below T_C because in TmCo$_2$ the intersublattice molecular field $H_{fd}^{(Co)}$ is less than the critical field of metamagnetic transition.

(ii) Two magnetic phase transitions were observed in TmCo$_2$. The higher transition at 3.8 K is the Curie temperature, while the lower one at 3.4 K represents the Tm moment rearrangement. The strong quadrupole–quadrupole interaction is assumed to be responsible for the low-lying phase transition. Both transitions are of first-order type. The purpose of the investigation of the less pure sample B was to demonstrate that the occurrence of two well separated transitions depends on the sample quality. Nevertheless also in this sample there is no long-range magnetic ordering of the Co d subsystem.

(iii) The substitution of Gd for Tm increases the (f–d) exchange interaction. The molecular field of the f–d interaction, $H_{fd}^{(Co)}$, induces a magnetic moment in the itinerant Co d subsystem of $Tm_{1-x}Gd_xCo_2$ for $x \geqslant 0.1$. The value of $M_{Co} \simeq 0.6\mu_B$ per Co for $x = 0.1$ is still considerably smaller than in other heavy RCo$_2$ compounds with higher $H_{fd}^{(Co)}$ and increases with x.

(iv) Due to the alignment of the anisotropic 4f shells of the Tm^{3+} ions in the crystal field below T_C there is a large anisotropic magnetostriction in TmCo$_2$, as well as in the Gd-substituted compounds. The estimated value of λ_{111} for TmCo$_2$ agrees well with those

for other heavy RCo_2 compounds within the single-ion theory.

(v) The existence of spin fluctuations in the paramagnetic temperature region in all these compounds ($LuCo_2$ included) has been proved by the temperature variation of transport phenomena. The pronounced negative curvature in ρ against T, as well as the uniform non-linear S against T dependence, are indications for a strong spin-fluctuation contribution to both the resistivity and the thermopower. The suppression of the spin fluctuations below T_C causes a large drop of the resistivity at T_C.

Acknowledgments

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