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2010 J. Phys.: Condens. Matter 22 136002

(http://iopscience.iop.org/0953-8984/22/13/136002)

J. Phys.: Condens. Matter **22** (2010) 136002 (6pp) doi:10.1088/0953-8984/22/13/136002

# Specific heat of $Gd_4Co_3$

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Received 25 December 2009, in final form 12 February 2010
Published 12 March 2010
Online at stacks.iop.org/JPhysCM/22/136002

**Abstract**

The specific heat ($C(T)$) of $Gd_4Co_3$ was measured in the temperature range 2–300 K and its magnetic contribution ($C_m(T)$) was determined using a new method that fits the electronic specific heat coefficient ($\gamma$) and the Debye temperature ($\theta_D$) by constraining the resulting magnetic entropy ($S_m(T)$) to saturate at temperatures far above the Curie temperature ($T_C$). $C_m(T)$ exhibits a low-temperature bump originating from thermal excitation of gapped spin waves, which is responsible for pronounced peaks, at ≈35 K, in both $C_m/T$ and the temperature derivative of the magnetic contribution to electrical resistivity ($d\rho_m/dT$). Apart from in the vicinity of $T_C$, an excellent global correlation was found between $C_m/T$ and $d\rho_m/dT$. Our results provide strong support for the consistency of the new method proposed for the determination of $C_m(T)$ and rule out any major role of short-range order on Gd moments or d-electron spin fluctuation effects in the paramagnetic phase. A comparative analysis with other methods used in similar compounds points to the need for a better evaluation of $C_m(T)$ in such compounds, especially in the magnetically ordered phase, where a deficient evaluation of $C_m/T$ has a larger impact on the $S_m(T)$ curve.

## 1. Introduction

Among the R–Co family, Gd–Co compounds are those that have the highest Curie temperatures due to the direct dependence of the 4f–3d exchange coupling on the spins of the 4f and 3d elements and due also to the fact that Gd has the highest spin among the rare earths. The 3d (Co)–5d (Gd) hybridization and the antiferromagnetic inter-sub-lattice 4f (Gd)–3d (Co) exchange coupling determine the magnetic state of Co atoms, which has a great influence on the magnetic and transport properties of these compounds. It is generally accepted that the 4f–3d exchange coupling splits the spin-up and spin-down 3d–5d hybridized bands, inducing a magnetic moment in the Co sub-lattice antiparallel to the Gd magnetic moment [1].

Moreover, Gd–Co compounds are also, at least in a first order approximation, free from crystal electric field effects, which simplifies the analysis of their magnetic behaviour. As the Co:Gd concentration ratio increases, the itinerant character of the magnetism is reinforced, whereas compounds with a low Co:Gd concentration ratio are expected to exhibit a magnetic behaviour much closer to the 4f localized magnetism typical of rare earths.

$Gd_4Co_3$ crystallizes in a hexagonal $Ho_4Co_3$ type structure of the $P6_3/m$ space group [2]. There are two rare-earth sites ($Gd_I$, $Gd_{II}$) with the same point symmetry 6h and three cobalt sites ($Co_I$ in 6h, $Co_{II}$ in 2d and $Co_{III}$ in 2b). The $Co_{III}$ site is partially filled at random by cobalt atoms. The unit cell, with parameters $a \approx 1.16$ nm and $c \approx 0.405$ nm, contains six $Gd_I$, six $Gd_{II}$, six $Co_I$, two $Co_{II}$ and 1.2 $Co_{III}$ atoms.

Having a low (3/4) Co:Gd concentration ratio, $Gd_4Co_3$ is a special system. It orders ferrimagnetically below $T_C \approx 220$ K [3–5] with the Co magnetic moments antiparallelly coupled to those of Gd. Below $T_{SR} \approx 163$ K [3] and somehow similarly to pure Gd [6], it exhibits a spin-reorientation (SR) process in which the Gd and Co magnetic moments tilt rigidly away from the initial ($c$-axis) easy magnetic direction. The effects of this SR process on the temperature dependence of the electrical resistivity were found to be very small and only noticeable in its temperature derivative [3]. A large

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magnetocaloric effect with negligible hysteretic loss was also reported for $Gd_4Co_3$ [7].

In this study, we focus on the temperature dependence of the specific heat of $Gd_4Co_3$ in order to further characterize its magnetic transitions and evaluate the role played by the Co 3d electrons, the Gd magnetic moments and the phonons.

## 2. Experimental details

A polycrystalline sample of $Gd_4Co_3$ has been prepared by arc-melting stoichiometric quantities of Gd and Co elements with 99.9% and 99.99% purities, respectively, under a purified argon atmosphere. In order to increase homogeneity, the ingot was remelted several times. Given the very small mass loss of the order of 0.04%, a final stoichiometric composition can be assumed. The resulting ingot was then encapsulated in a quartz tube, under an argon atmosphere, and annealed at 600 °C for 2 h, then at 635 °C for 24 h and at 650 °C for 48 h. X-ray diffraction on the annealed material revealed a single phase with the $Ho_4Co_3$ crystal structure [2].

Specific heat measurements were made on samples of $2.5 \times 2.5 \times 1.5$ mm$^3$, in the temperature range 2–300 K, with a Quantum Design PPMS calorimeter that uses a two-relaxation-time technique, and data were always collected during sample cooling. The intensity of the heat pulses was calculated to produce a variation in the temperature bath between 0.5% (at low temperatures) and 2% (at high temperatures). Experimental errors in all measurements presented here were typically lower than 1%.

## 3. Results and discussion

Figure 1 shows the specific heat curve, $C(T)$, of $Gd_4Co_3$. The $C(T)$ curve clearly exhibits two peaks centred at the temperatures $T_C \approx 216.3$ K and $T_{SR} \approx 159.0$ K associated, respectively, with the transition from the paramagnetic to the ferrimagnetic phase and the SR transition. These temperatures differ from those obtained previously [3] through magnetic measurements (221 K and 163 K, respectively) by about 5 K and 4 K, in the case of $T_C$ and $T_{SR}$, respectively. Such large temperature differences cannot be attributed to thermometry errors. Effects of sample polycrystallinity may play an important role in the vicinity of the magnetic transitions but cannot account for the observed differences, since they would be incompatible with the sharp transitions observed in low-field isofield magnetization curves of $Gd_4Co_3$ [3]. We point out that the critical temperatures obtained from magnetic measurements closely match the temperatures of the inflexion points just above the peaks of the $C(T)$ curve. This phenomenon is not unusual since it has been observed in numerous Gd based intermetallic compounds (for the cases of, for example, $GdCu_2Si_2$, $GdNi_2Si_2$, $GdGa_2$ and $GdCu_5$, see [8]).

The specific heat of $Gd_4Co_3$ can be analysed assuming independent and additive contributions from the electronic ($C_e$), phonon ($C_{ph}$) and magnetic ($C_m$) subsystems:

$$C(T) = C_e(T) + C_{ph}(T) + C_m(T). \quad (1)$$

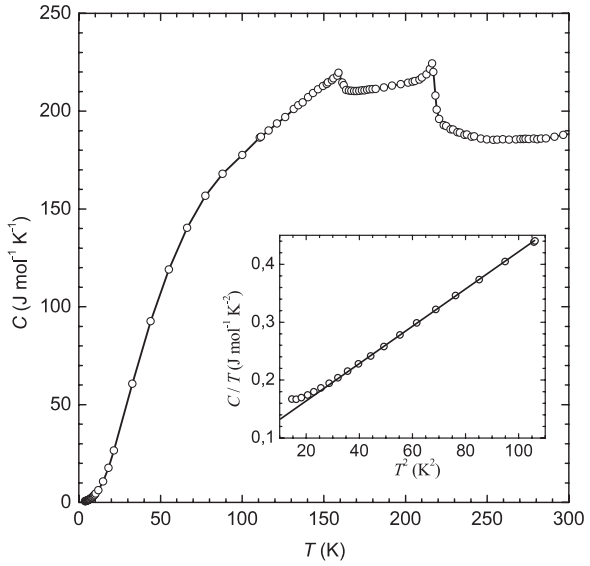


**Figure 1.** Temperature dependence of the specific heat of $Gd_4Co_3$. The inset shows the low-temperature plot of $C(T)/T$ versus $T^2$.

In order to determine $C_m(T)$ from the measured $C(T)$ data, both $C_e(T)$ and $C_{ph}(T)$ contributions need to be properly evaluated. The conduction electron specific heat is given by $C_e(T) = \gamma T$, where $\gamma$ is the electronic specific heat coefficient, which can be determined through the low-temperature $C(T)/T$ versus $T^2$ plot (see inset of figure 1). For $T \ll \theta_D$, where $\theta_D$ is the Debye temperature, we have [9] $C/T = \gamma + \beta T^2$, where $\beta = 12\pi^4 NR/(5\theta_D^3)$, $N$ is the number of atoms per formula unit ($N = 7$ in our case) and $R \approx 8.314$ J mol$^{-1}$ K$^{-1}$ is the ideal gas constant. From the fitted straight line, we found $\gamma = 110.0 \pm 0.5$ mJ mol$^{-1}$ K$^{-2}$ and $\theta_D = 164.3 \pm 0.5$ K. As will be shown below, these low-temperature values of $\gamma$ and $\theta_D$, hereafter denoted by $\gamma^{LT}$ and $\theta_D^{LT}$, respectively, do not describe satisfactorily the behaviour of $C_e(T)$ and $C_{ph}(T)$ in the whole temperature range of the experimental data.

As seen in the inset of figure 1, the $C(T)/T$ versus $T^2$ plot exhibits a small upturn below 5 K. Such an effect is related to a non-Fermi liquid behaviour whose full characterization requires further investigation at lower temperatures.

Considering the nonmagnetic and isostructural compound $Y_4Co_3$ as a reference for the lattice specific heat of $Gd_4Co_3$, we may use the two-Debye function method described in [8, 10] to estimate, from the different molar masses of Gd ($M_{Gd}$) and Y ($M_Y$), a Debye temperature ratio

$$r = \frac{\theta_D(Gd_4Co_3)}{\theta_D(Y_4Co_3)} = \left(\frac{4M_Y^{3/2} + 3M_{Co}^{3/2}}{4M_{Gd}^{3/2} + 3M_{Co}^{3/2}}\right)^{1/3} \approx 0.80. \quad (2)$$

This value is in good agreement with the ratio $r_{exp} \approx 0.77$ of the experimentally determined Debye temperatures $\theta_D^{LT}(Gd_4Co_3) \approx 164.3$ K and $\theta_D^{LT}(Y_4Co_3) \approx 212.0$ K [11], confirming the consistency of the low-temperature data analysis.

The determination of the magnetic specific heat ($C_m = C - C_e - C_{ph}$) of $Gd_4Co_3$ has been performed using four

**Table 1.** Models used in this work to determine the nonmagnetic specific heat of $Gd_4Co_3$. Values of $\gamma$ and $\theta_D$ have units of mJ mol$^{-1}$ K$^{-2}$ and K, respectively.

| Method | Model | Fixed parameters | Adjustable parameters |
|---|---|---|---|
| I | $\gamma^{LT}(Gd_4Co_3)T + Nf_D(\theta_D^{LT}(Gd_4Co_3)/T)$ | $\gamma^{LT}(Gd_4Co_3) = 110.0$<br>$\theta_D^{LT}(Gd_4Co_3) = 164.3$ | None |
| II | $\gamma^{LT}(Y_4Co_3)T + Nf_D(\theta_D^{LT}(Gd_4Co_3)/T)$ | $\gamma^{LT}(Y_4Co_3) = 38.4$<br>$\theta_D^{LT}(Gd_4Co_3) = 164.3$ | None |
| III | $\gamma^{LT}(Y_4Co_3)T + C_{ph}^{(Y_4Co_3)}(T/\gamma_{exp})$ | $\gamma^{LT}(Y_4Co_3) = 38.4$<br>$r_{exp} = 0.77$ | None |
| IV | $\gamma T + Nf_D(\theta_D/T)$ | None | $\gamma = 57.2$<br>$\theta_D = 209$ |

**Table 2.** Models used in other works to determine the nonmagnetic specific heat of compounds similar to $Gd_4Co_3$. Values of $\gamma$ and $\theta_D$ have units of mJ mol$^{-1}$ K$^{-2}$ and K, respectively.

| Reference | Compound | Model | Parameters | Method |
|---|---|---|---|---|
| [12] | $Y_3Co$ | $\gamma T + Nf_D(\theta_D/T)$ | $\gamma = 15, \theta_D = 223$ | I |
| | $Gd_3Co$ | $\gamma(Y_3Co)T + Nf_D(\theta_D/T)$ | $\gamma(Y_3Co) = 15, \theta_D = 157$ | II |
| [13] | $Y_3Co$ | $\gamma T + Nf_D(\theta_D/T)$ | $\gamma = 15, \theta_D = 234$ | I |
| | $Y_3Ni$ | $\gamma T + Nf_D(\theta_D/T)$ | $\gamma = 41.5, \theta_D = 234$ | I |
| | $Gd_3Co$ | $\gamma(Y_3Co)T + Nf_D(\theta_D/T)$ | $\gamma(Y_3Co) = 15$<br>$\theta_D = r\theta_D(Y_3Co) = 181$ K | II, III |
| [14] | $Gd_3Rh$ | $\gamma(Y_3Rh)T + Nf_D(\theta_D/T)$ | $\gamma(Y_3Rh) = 11$<br>$\theta_D(Gd_3Co) = 157$ K<br>$\theta_D = r\theta_D(Gd_3Co) = 151$ K | II, III |

different methods (I, II, III, IV) with quite different results. In table 1, we summarize the corresponding models for the nonmagnetic contributions, including their fixed or adjustable parameters. Methods I, II and IV calculate the phonon contribution using the Debye model, according to which

$$C_{ph}(T) = Nf_D\left(\frac{\theta_D}{T}\right) = 9\,NR\left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x\,dx}{(e^x-1)^2} \tag{3}$$

where $f_D(\theta_D/T)$ is the Debye function.

Method I calculates directly $C_e$ and $C_{ph}$ taking $\gamma = \gamma^{LT}(Gd_4Co_3)$ and $\theta_D = \theta_D^{LT}(Gd_4Co_3)$. In method II, the electronic specific heat is that of $Y_4Co_3$ whereas the phononic one is calculated using the Debye function with $\theta_D = \theta_D^{LT}(Gd_4Co_3)$. Method III uses the specific heat of $Y_4Co_3$ [11] as a reference for the nonmagnetic specific heat of $Gd_4Co_3$. For the phonon contribution, a proper temperature normalization with the experimentally determined ratio $r_{exp}$ was made to transform $C_{ph}^{(Y_4Co_3)}$ into $C_{ph}^{(Gd_4Co_3)}$. It should be noticed that these three methods have been used often for the determination of $C_e + C_{ph}$ of similar compounds (see table 2 and references therein).

Methods I and II appear to be totally inadequate since they produce unphysical negative values of $C_m(T)$ over wide temperature intervals. Method III introduces an important qualitative improvement, since $C_m(T) > 0$ in the whole temperature range (see figure 2). This indicates that $C_{ph}^{(Gd_4Co_3)}$ is better described by taking as reference the temperature-normalized curve of $C_{ph}^{(Y_4Co_3)}$ rather than a Debye function with a low-temperature estimate for $\theta_D(Gd_4Co_3)$. However, the

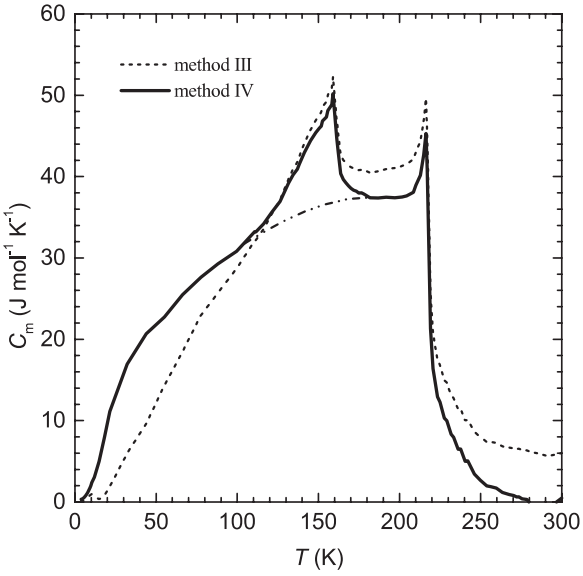


**Figure 2.** Temperature dependence of the magnetic specific heat of $Gd_4Co_3$ as obtained through models III and IV (see the text for details). The dash–dotted curve sketches the hypothetical magnetic background of the SR anomaly.

$C_m(T)$ curve obtained through method III still exhibits some features that may have no intrinsic origin. In this respect, we mention the quasi-linear variation of $C_m$ between 20 and 160 K, which is rather unusual for a Gd compound, where a characteristic low-temperature bump is often observed [8, 15]. Moreover, it is worth mentioning the persistence of appreciable

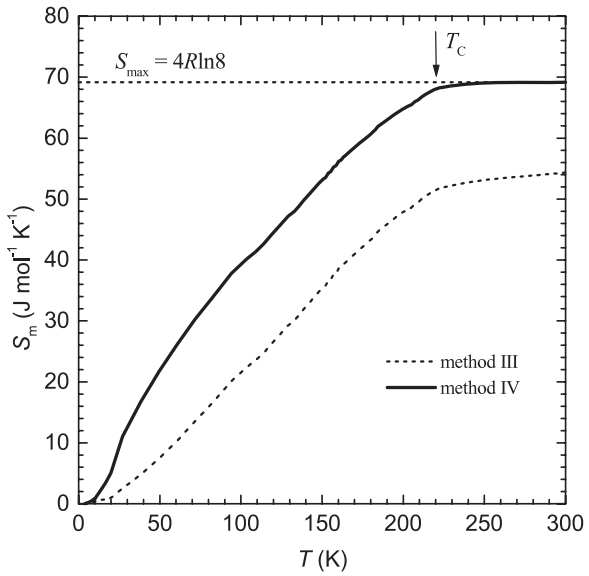


**Figure 3.** Temperature dependence of the magnetic entropy of $Gd_4Co_3$ as obtained through models III and IV.

values of $C_m$ for $T > T_C$ without a clear sign for its vanishing above 300 K. Despite this specific heat excess above $T_C$, the numerically calculated magnetic entropy, $S_m(T) = \int_0^T C_m(T')/T'dT'$, exhibits anomalously low values. Even at 300 K this $S_m(T)$ reaches only 79% of its maximum value, $S_m^{max} = 4R\ln 8$, corresponding to 4 $Gd^{3+}$ free ions (see figure 3). The weak and quasi-linear variation of $S_m(T)$ observed above $T_C$, which is responsible for a change of only 3% of $S_m^{max}$, points to saturation at $S_m^{max}$ for temperatures much higher than 300 K, which is probably wrong.

Large deficits of the order of 20–40% in magnetic entropy above $T_C$ (or $T_N$ for antiferromagnets) were also reported for several similar compounds and attributed to the existence of short-range correlations between Gd magnetic moments and to spin fluctuations in the d-electron subsystem enhanced by the 4f–*n*d coupling (for the cases of $Gd_3Co$ and $Gd_3Rh$, see [12, 13] and [14], respectively). We notice that such results were obtained using essentially method II, which failed utterly with $Gd_4Co_3$. In fact, the electrical resistivity of $Gd_4Co_3$ shows a quasi-linear temperature dependence near room temperature [3], which is incompatible with significant short-range correlations or spin fluctuation effects at temperatures well above $T_C$, as the results of method III might suggest.

In order to overcome the inadequacies of methods I, II and (to a lesser extent) of method III, we propose a new method (IV) which implicitly assumes that, for temperatures $T \gg T_C$, the magnetic entropy should saturate at its maximum value. As mentioned above, in the case of $Gd_4Co_3$, this assumption is physically supported by the electrical resistivity results. A fundamentally more significant consistency of this model, which is unmatched by other models, will be presented below.

The constraint on the saturation of $S_m(T)$ is implemented on the model $C_m(T) = C(T) - \gamma T - Nf_D(\theta_D/T)$ by minimizing the merit function

$$\psi = \sum_k \left(1 - \frac{S_m(T_k)}{S_m^{max}}\right)^2 \tag{4}$$

with respect to the parameters $\gamma$ and $\theta_D$. In equation (4), the sum runs for $k$ satisfying the condition 280 K $\leqslant T_k \leqslant$ 300 K, which ensures that $S_m(T_k) \approx S_m^{max}$ should apply, at least approximately, if thermal disorder of the Gd magnetic moments is the only or dominant mechanism to be considered in the paramagnetic phase. For other rare-earth compounds exhibiting crystal electric field (CEF) effects, this method still applies provided that the corresponding CEF splittings (in K) are much lower than the maximum temperature of the experimental specific heat data (300 K, in our case).

The fitting of model IV provided the parameters $\gamma = 57.2$ mJ mol$^{-1}$ K$^{-2}$ and $\theta_D = 209$ K, which are considerably different from $\gamma^{LT}(Gd_4Co_3)$ and $\theta_D^{LT}(Gd_4Co_3)$, respectively. We can estimate a reference value of $\theta_D(Gd_4Co_3)$ from the known values $\theta_D(Gd) = 187$ K [16] and $\theta_D(Gd) = 385$ K [17]. Applying the two-Debye function method [8, 10], we have

$$\frac{7}{[\theta_D(Gd_4Co_3)]^3} = \frac{4}{[\theta_D(Gd)]^3} + \frac{3}{[\theta_D(Co)]^3} \tag{5}$$

from which we obtain $\theta_D(Gd_4Co_3) = 219$ K. This reference value is only 5% higher than the value obtained through the fitting of model IV.

As seen in figures 2 and 3, the major pitfalls found in methods I, II and III are absent in method IV. A low-temperature bump in $C_m(T)$ is clearly seen below approximately 100 K. In complete agreement with our previous work [3], above approximately 100 K the anomaly in $C_m(T)$ begins, corresponding to the SR process. Since such intrinsic features of the known magnetic behaviour of $Gd_4Co_3$ are not observed in the results of any of the previous methods, we may conclude that method IV provides a better approximation to $C_m(T)$. Actually, those features can be used to check the consistency of the different approaches used in the determination of $C_m(T)$.

The magnetic entropy saturates at temperatures just slightly above $T_C$, well below the imposed temperature range for the condition $S_m(T_k) \approx S_m^{max}$ to be valid. In fact, the entropy change associated with the tail of $C_m(T)$ in the paramagnetic region amounts to only 2% of the total variation of the magnetic entropy. This is, presumably, the maximum possible contribution ascribable to short-range order on Gd moments and/or d-electron spin fluctuations above $T_C$. We notice that this picture agrees with the quasi-linear temperature dependence of the electrical resistivity of $Gd_4Co_3$ observed above $T_C$ [3], which can be fully understood as a simple effect of the scattering of electrons by phonons [9]. It should be remarked that the significant difference found between the $S_m(T)$ curves corresponding to methods III and IV sets in already at low temperatures, where method IV provides higher values for $C_m(T)$.

Figure 4 shows simultaneous plots of $C_m/T$ from methods III and IV and of the temperature derivative of the magnetic contribution to the electrical resistivity ($d\rho_m/dT$)

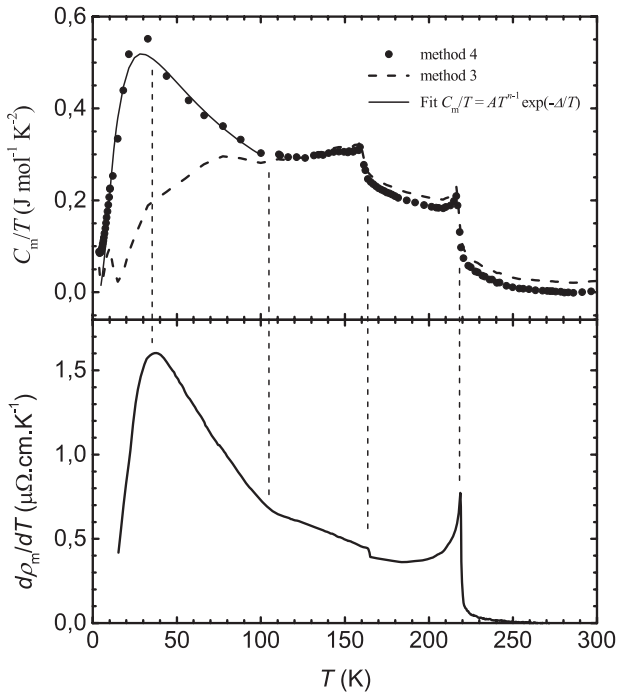


**Figure 4.** Simultaneous plots of $C_m/T$ from methods III and IV (top panel) and of $d\rho_m/dT$ (bottom panel) of $Gd_4Co_3$. The vertical dashed lines mark common anomalies in both plots. The solid line in the top panel marks the fit $C_m/T = AT^{n-1}\exp(-\Delta/T)$ for temperatures below 100 K (see the text).

of $Gd_4Co_3$ [18]. In the case of method IV, there is a very good correlation between these two quantities in the whole temperature range. In the case of method III, however, the correlation exists just for temperatures above 100 K. Below 100 K, only method IV is able to show a well defined and pronounced peak in $C_m/T$ at $T \approx 35$ K that is also observed in $d\rho_m/dT$. Such an intrinsic peak in $d\rho_m/dT$ is likely related to thermal excitation of gapped spin waves and their effect on electron conduction through a strong s–d scattering mechanism typical of d-band magnetic systems [19, 20].

It should be noticed that for a ferrimagnet with a gapped spin wave spectrum which, in the case of $Gd_4Co_3$, could originate from anisotropic exchange interactions, $C_m(T)$ increases exponentially at low temperatures according to a dependence of the type $C_m(T) \propto T^n \exp(-\frac{\Delta}{T})$. Here, $\Delta$ is the associated gap (in kelvins) and $n$ is an exponent whose value is $1/2$ for an easy plane anisotropy and $-1/2$ for an easy axis anisotropy [21]. In fact, the existence of a peak in $C_m(T)/T$ indicates necessarily that $n < 1$. Since $Gd_4Co_3$ exhibits an SR transition dictated by the competition between axial and planar anisotropies, it is possible that $n$ may lie between these limits. This is confirmed by the numerical fit to the peak in $C_m(T)/T$, as shown by the solid line in the top graph of figure 4 for temperatures up to 100 K, which provides the values $n = -0.06 \pm 0.08$ and $\Delta = 31 \pm 2$ K.

The excellent correlation found between the $C_m/T$ and $d\rho_m/dT$ curves shows unambiguously the consistency and validity of method IV in the determination of $C_m(T)$ in $Gd_4Co_3$. A question naturally arises regarding the origin of this correlation since, according to Fisher and Langer [22], the same spin–spin correlation function is involved in the magnetic energy and relaxation time associated with electron scattering by spin fluctuations. Therefore, $d\rho_m/dT$ should correlate with $C_m$, as generally observed, rather than with $C_m/T$. In fact, the expected correlation seems to happen in our data only for the near vicinity of the transition at $T_C$. So far, to our knowledge, the global $C_m/T$ versus $d\rho_m/dT$, or equivalently $S_m$ versus $\rho_m$, correlation has been reported only for the antiferromagnetic heavy-fermion compound $CeRhIn_5$ [23] and still remains unexplained.

## 4. Conclusion

The specific heat of $Gd_4Co_3$ has been measured and analysed in order to extract its magnetic contribution ($C_m$). For this purpose, we have tested several models of the nonmagnetic specific heat (electronic plus phononic) that have been applied to other related compounds (methods I, II and III). None of these models was able to describe properly intrinsic features of the known magnetic and electrical transport behaviour of $Gd_4Co_3$. Apparently, the importance of this type of detailed consistency check has been underestimated in the determination of the magnetic specific heat of other compounds.

In order to avoid the inadequacies of methods I, II and III, we developed a new method (IV) that constrains the resulting magnetic entropy ($S_m$) to saturate at its maximum value, $S_m^{max} = 4R \ln 8$, corresponding to 4 $Gd^{3+}$ free ions, at temperatures far above $T_C$, and takes both $\gamma$ and $\theta_D$ as fitting parameters. To our knowledge, this is a completely original method for the determination of $C_m(T)$.

Several important results evidenced only through this method confirm its high consistency in the case of $Gd_4Co_3$. A low-temperature bump characteristic of Gd compounds is observed below 100 K. Such a bump is associated with pronounced peaks in both $C_m/T$ and $d\rho_m/dT$ curves at about 35 K. We showed that this behaviour could originate from thermal excitation of gapped spin waves.

A rather small (2%) change in magnetic entropy above $T_C$ and up to saturation was deduced, which rules out any major role of short-range order on Gd moments or d-electron spin fluctuation effects in the paramagnetic phase. We notice that method IV constrains the saturation of $S_m$ only for 280 K $\leqslant T \leqslant$ 30 K, so that the observed value of $\Delta S_m(T > T_C)$ is not artificially imposed. This result complies fully with the previously reported quasi-linear temperature dependence of the electrical resistivity of $Gd_4Co_3$ [3]. In some similar Gd compounds, deficits of 20–40% in magnetic entropy at $T_C$ or $T_N$ [12–14] were reported and attributed to short-range order on Gd moments and d-electron spin fluctuations. However, in all cases, the increase of $S_m$ in the paramagnetic phase is too small to drive it close to $S_m^{max}$, even for temperatures far above $T_C$ or $T_N$. It should be pointed out that such low values of $S_m$ resulted from the application of a method equivalent to method II of this work, which provided unphysical results for $Gd_4Co_3$. Thus it is possible that, in such cases, the application of method IV proposed in this work could provide a better

description of $C_m(T)$ in the ordered phase, precisely where a deficient evaluation of $C_m/T$ has a larger impact on the $S_m(T)$ curve.

An excellent global correlation between $C_m/T$ and $d\rho_m/dT$ was found, except in the vicinity of $T_C$, where the $C_m$ versus $d\rho_m/dT$ correlation predicted by Fisher and Langer [22] theory is a better approximation. Further studies are required in order to investigate the possible origin of this non-standard behaviour.

It should be noticed that, in contrast to the predictions of the Debye model, low-temperature peaks in $C_{ph}/T^3$ versus $T$ curves of amorphous and crystalline metals were shown to result from the excitation of low-frequency vibrations of unclear origin [24]. Such peaks have amplitudes of up to five times the value given by the Debye model. In the case of $Gd_4Co_3$ [3], however, it is found that $[d\rho/dT(35\ K)]/[d\rho/dT(300\ K)] \approx 33$, whereas the Bloch–Grüneisen model [25] predicts a value for this ratio of the order of unity if the low-temperature peak is of phonon origin. Given the observed globally good correlation between $d\rho_m/dT$ and $C_m/T$, if the peak in $C_m/T$ was due to a severe inadequacy of the Debye model used in the determination of $C_m(T)$ to describe low-frequency vibrations, then we would expect its peak amplitude to be about 30 times higher than the value predicted by the Debye model and, consequently six times higher than the above quoted maximum peak amplitude associated with low-frequency vibrations. This observation brings further support to the idea that the low-temperature peak in $C_m/T$ is of magnetic origin.

## Acknowledgments

This work was financed by the POCTI/2000/CTM/36224—Sapiens FCT project and the ERBFMGECT—950072 TMR program. O F de Lima and J Lopez acknowledge the financial support from the Brazilian science agencies FAPESP and CNPq.

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