

## Spin fluctuations in $\text{Gd}_3\text{Rh}$ induced by f–d exchange: the influence on the $T$ -linear specific heat

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2003 J. Phys.: Condens. Matter 15 531

(<http://iopscience.iop.org/0953-8984/15/3/317>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.119

The article was downloaded on 19/05/2010 at 06:29

Please note that [terms and conditions apply](#).

## Spin fluctuations in Gd<sub>3</sub>Rh induced by f–d exchange: the influence on the *T*-linear specific heat

N V Baranov<sup>1,2,5</sup>, K Inoue<sup>3</sup>, H Michor<sup>4</sup>, G Hilscher<sup>4</sup> and A A Yermakov<sup>1,2</sup>

<sup>1</sup> Institute of Metal Physics, Russian Academy of Science, 620219 Ekaterinburg, Russia

<sup>2</sup> Institute of Physics and Applied Mathematics, Ural State University, Lenin Avenue 51, 620083 Ekaterinburg, Russia

<sup>3</sup> Institute for Molecular Science, Myodaiji, Okazaki 444, Japan

<sup>4</sup> Institut für Festkörperphysik, TU Wien, A-1040 Wien, Austria

E-mail: nikolai.baranov@usu.ru

Received 3 October 2002

Published 13 January 2003

Online at [stacks.iop.org/JPhysCM/15/531](http://stacks.iop.org/JPhysCM/15/531)

### Abstract

The results of specific heat, magnetization and magnetic susceptibility measurements for the antiferromagnetic (AF) compound Gd<sub>3</sub>Rh are presented. Below its Néel temperature  $T_N = 112$  K, this compound exhibits a field-induced phase transition from the AF to the ferromagnetic state in a relatively small magnetic field ( $\sim 0.4$  T). Specific heat measurements revealed a giant enhancement of the coefficient of the *T*-linear specific heat in Gd<sub>3</sub>Rh ( $\gamma = 118$  mJ mol<sup>-1</sup> K<sup>-2</sup>) in comparison with that observed for the isostructural nonmagnetic partner Y<sub>3</sub>Rh ( $\gamma = 11$  mJ mol<sup>-1</sup> K<sup>-2</sup>). An anomalous behaviour of the heat capacity as well as a set of peculiarities of magnetic properties in Gd<sub>3</sub>Rh are associated with the existence of spin fluctuations induced by f–d exchange interaction in the d-electron subsystem that arises from features of the crystal and electronic structure of the R<sub>3</sub>M-type compounds.

### 1. Introduction

Some rare-earth compounds of an R<sub>3</sub>M type (M = Co, Ni) have revealed an unusual behaviour of their heat capacity. In particular, a strong dependence of the coefficient  $\gamma$  of the *T*-linear specific heat on the kind of R ion was observed. The  $\gamma$ -value was found to be about 110 mJ mol<sup>-1</sup> K<sup>-2</sup> for Gd<sub>3</sub>Co [1, 2] and 100 mJ mol<sup>-1</sup> K<sup>-2</sup> for Gd<sub>3</sub>Ni [3], whereas it reaches only 15 and 14 mJ mol<sup>-1</sup> K<sup>-2</sup> for isostructural Y<sub>3</sub>Co [2, 3] and Y<sub>3</sub>Ni [4]. A giant enhancement of  $\gamma$  up to 380 and 425 mJ mol<sup>-1</sup> K<sup>-2</sup> was found to exist in the vicinity of the onset of long-range magnetic order in pseudobinary systems (Gd<sub>1-x</sub>Y<sub>x</sub>)<sub>3</sub>Co and (Gd<sub>1-x</sub>Y<sub>x</sub>)<sub>3</sub>Ni [3]. Moreover, when analysing the magnetic contribution to the entropy of (Gd<sub>1-x</sub>Y<sub>x</sub>)<sub>3</sub>Co compounds it was shown that the magnetic entropy does not reach the theoretical value  $S_m = 3R(1-x) \ln 8$  even

<sup>5</sup> Author to whom any correspondence should be addressed.

at temperatures of about two times the magnetic ordering temperature. The above properties, which seem to be unusual for Gd–Co and Gd–Ni pseudobinaries, were attributed to the strong influence of f electrons of R ions on the d-electron subsystem of the transition metal that results in the presence of spin fluctuations induced by the f–d exchange interaction.

Within the series of R–M intermetallics, the  $R_3M$  compounds have the highest R content and crystallize in the orthorhombic  $Fe_3C$ -type structure when M is a 3d (Co, Ni), 4d (Rh, Pd), or 5d (Ir, Pt) transition metal with an almost full d band. The crystal structure of  $R_3M$  compounds consists of trigonal prisms, the corners of which are occupied by R ions. The transition metal atoms are located within such prisms. The high rare-earth content in  $R_3M$  leads to a transfer of 5d (4d in the case of Y) electrons of R ions to the unfilled d band that results in the absence of magnetic moments on M atoms. According to an x-ray photoemission study [5] the electronic structure of  $Gd_3Rh$  is characterized by a significantly narrower Rh 4d band (about 2 eV) in comparison with that of pure rhodium (about 5.5 eV). This is attributed to the reduced overlap of the 4d orbitals owing to the large Rh–Rh distance ( $\sim 4$  nm) in the  $Fe_3C$ -type lattice. The Fermi level in  $Gd_3Rh$  is located in the region with positive curvature above the top of the 4d states hybridized with 5d states of Gd. Note that such peculiarities of the electronic structure were observed for other  $R_3M$  compounds with  $M = Ni, Ir$  [5, 6].

The fact that M ions are surrounded in the  $Fe_3C$ -type lattice by rare-earth ions, together with the large distance between M ions situated in the neighbour prisms, implies the presence of strong correlations between 4f electrons of R ions and d electrons of transition metal ions, and significant localization of spin fluctuations in the d-electron subsystem in  $R_3M$  compounds.

As to the magnetic properties of  $Gd_3Rh$ , the previous study has shown that this compound can be classified as an antiferromagnet [5]. The Néel temperature of  $Gd_3Rh$ ,  $T_N = 112$  K, lies between the ordering temperatures of  $Gd_3Co$  (131 K; see [1]) and  $Gd_3Ni$  (100 K; see [7]).

In the present study we focus on the specific heat behaviour of the  $Gd_3Rh$  compound, to verify a possible influence of spin fluctuations.

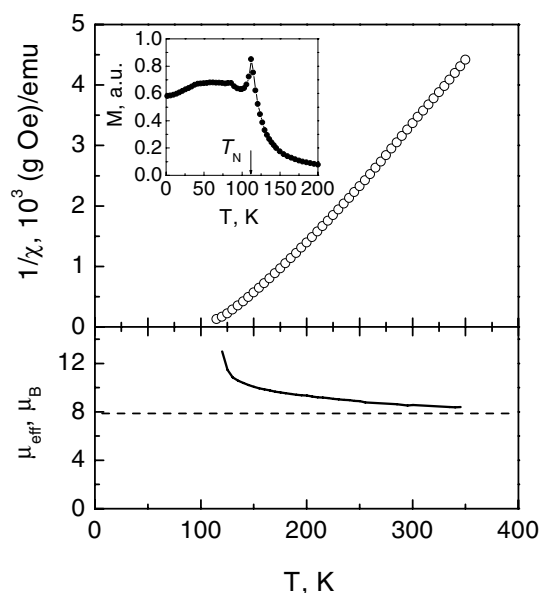
## 2. Experimental details

The  $Gd_3Rh$  and  $Y_3Rh$  compounds were obtained by arc melting in a helium atmosphere using gadolinium and yttrium of 99.9% purity and rhodium of 99.99% purity respectively. The ingots were remelted several times to achieve good homogeneity of the samples. Using x-ray diffraction, the crystal structure of the samples was found to be of  $Fe_3C$  type. The traces of foreign phases (<3%) were detected by using a metallographic method. It was found that annealing at 600 °C for several days does not appreciably affect the properties of  $R_3Rh$  samples. Note: this is a common feature of  $R_3M$  compounds.

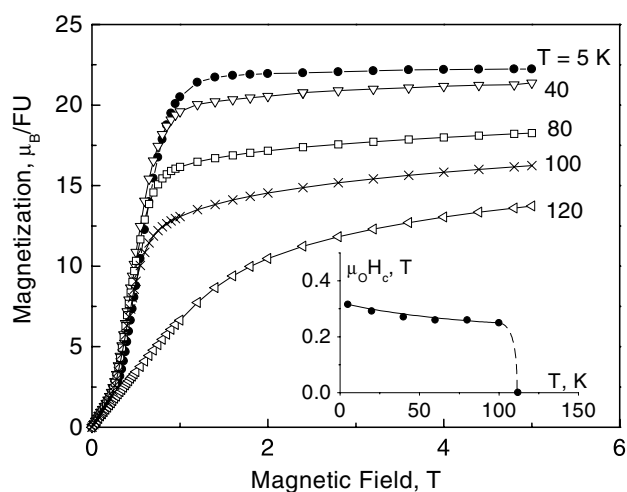
The magnetization measurements were made on the polycrystalline sample of  $Gd_3Rh$  by using a SQUID magnetometer (Quantum Design, USA) in the temperature range 2–350 K. Specific heat measurements in the temperature range 3–140 K in zero magnetic field were carried out on samples with a typical mass of 500 mg employing an adiabatic step-heating technique. The sample holder consists of a thin sapphire disc with a strain gauge heater and a calibrated CERNOX temperature sensor. The addenda calibration was performed with an NBS copper standard. The accuracy of the experiment is better than 1% below 100 K and 1–3% above.

## 3. Results and discussion

To examine the magnetic state of the  $Gd_3Rh$  sample we measured the temperature dependence of the magnetization at low (0.01 T) dc magnetic field in the temperature range 2–200 K, field dependences of the magnetization at different temperatures in magnetic fields up to 5 T, as well



**Figure 1.** Temperature dependences of the reciprocal magnetic susceptibility ( $\chi^{-1}$ ) and effective magnetic moment ( $\mu_{eff}$ ) for Gd<sub>3</sub>Rh. The inset shows the temperature dependence of the magnetization measured at  $\mu_0 H = 0.01$  T.



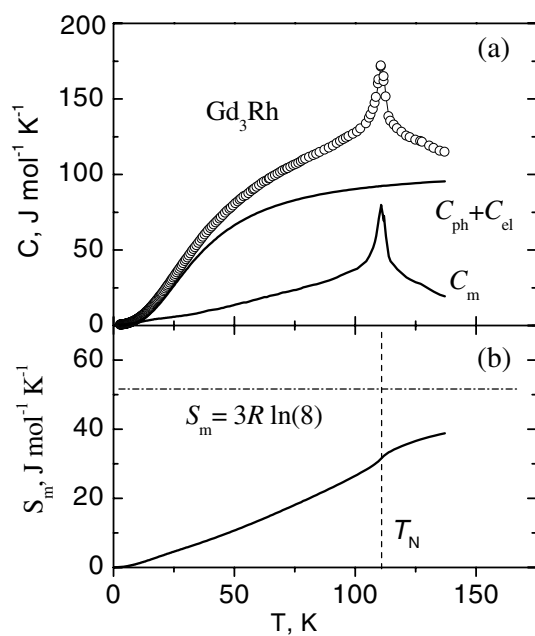
**Figure 2.** Magnetization curves measured for Gd<sub>3</sub>Rh at various temperatures. The inset shows the temperature dependence of the critical transition field.

as the temperature dependence of the magnetic susceptibility in the field 1 T in the paramagnetic region (120–350 K). All these results are displayed in figures 1 and 2. The sharp peak at  $T = 112$  K in the  $M(T)$  dependence (see the inset in figure 1) indicates the Néel temperature of Gd<sub>3</sub>Rh, which is consistent with data in [5]. As to the magnetic susceptibility, its temperature dependence within the temperature interval 120–350 K cannot be reasonably well described by the expression  $\chi(T) = \chi_0 + C/(T - \Theta_p)$ , considering that the  $C$ -value and consequently

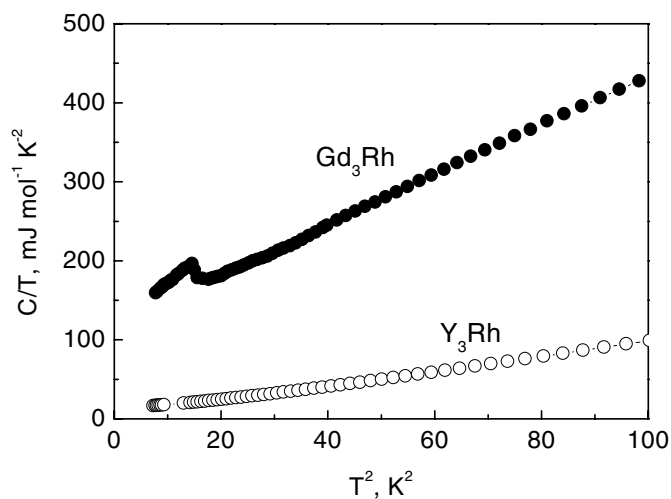
the effective moment  $\mu_{eff}$  do not change with temperature. The deviation of  $\chi(T)$  from the Curie–Weiss law cannot be ascribed in this case to crystal field effects because of the S state of the Gd ions. Assuming a possible change of the  $\mu_{eff}$ -value due to the presence of short-range correlations and a spin fluctuation contribution, we have calculated  $\mu_{eff}(T)$  using the Curie law. The effective magnetic moment per gadolinium is found to be significantly temperature dependent (see figure 1) and exceeds the value of  $\mu^{Gd^{3+}} = g[J(J+1)]^{1/2} = 7.94 \mu_B$  for the free Gd ion even at high temperatures. The  $\mu_{eff}$ -value approaches  $8.4 \mu_B$  at  $T = 350$  K. Such an enhancement over  $\mu^{Gd^{3+}}$  may result from short-range correlations between Gd magnetic moments and spin fluctuation effects in the d-electron subsystem influenced by the Gd ions. Note that in [5] the excess  $\Delta\mu = \mu_{eff} - \mu_0 = 0.55 \mu_B$  was found to exist at temperatures up to 800 K.

An antiferromagnetic (AF) character of the magnetic ordering in Gd<sub>3</sub>Rh is strongly indicated by the magnetization curves measured below  $T_N$  (figure 2). Like for the isostructural compounds Gd<sub>3</sub>Co and Gd<sub>3</sub>Ni, the  $M(H)$  dependences for Gd<sub>3</sub>Rh show an abrupt increase of the magnetization when the field increases above the critical value  $H_c$ . We attribute such behaviour to the metamagnetic phase transition from the AF order to the ferromagnetic (F) alignment of Gd magnetic moments since the saturation magnetization per Gd ion reaches  $7.2 \mu_B$ . This value exceeds that expected for the free Gd<sup>3+</sup> ion ( $gJ = 7 \mu_B$ ). The additional moment can be ascribed to an itinerant electron contribution associated with rhodium. The value of the critical field of the AF–F transition in Gd<sub>3</sub>Rh ( $\sim 0.4$  T) is lower than in Gd<sub>3</sub>Co ( $\sim 0.8$  T [1]) and in Gd<sub>3</sub>Ni ( $\sim 4$  T [7]) which suggests a smaller energy difference between AF and F phases in Gd<sub>3</sub>Rh. The shape of the magnetization curve of Gd<sub>3</sub>Rh is similar to the  $M(H)$  dependence for polycrystalline samples of Gd<sub>3</sub>Co [1, 7]. The measurements of the magnetization for single-crystalline samples of spherical shape have shown that in the vicinity of the AF–F transition the slopes of the  $M(H)$  curves measured along the *b*- and *c*-axes of Gd<sub>3</sub>Co agree very well with the demagnetizing factor. This prompted us to suggest that the evolution of the AF–F transition along these axes occurs by nucleation of the F phase within the AF matrix followed by motion of the interphase boundaries, like in other metamagnets [8]. The magnetization measured along the *a*-axis of Gd<sub>3</sub>Co was found to increase gradually with increasing field. Such behaviour was attributed to rotation of Gd magnetic moments. An analogous behaviour of the magnetization—step-like increases at critical fields along the *b*- and *c*-axes and a gradual increase when the field was applied along the *a*-axis—was also observed by Tristan *et al* (see [7]) for single-crystal Gd<sub>3</sub>Ni. One can, therefore, assume that the process of magnetization of the polycrystalline sample Gd<sub>3</sub>Rh in the vicinity of the AF–F transition involves all of the above-mentioned processes: nucleation of a new phase, motion of the interphase boundaries, and rotation of magnetic moments in the field direction. Unfortunately, the magnetic structure of Gd<sub>3</sub>Rh, like those of other Gd<sub>3</sub>M compounds, is still unknown because of the very large absorption of neutrons by Gd. The complicated magnetization behaviour revealed by measurements on Gd<sub>3</sub>Co and Gd<sub>3</sub>Ni single crystals was attributed to the presence of complex noncollinear magnetic structures in these compounds [1, 7]. Bearing in mind a giant magnetoresistance effect ( $\Delta\rho/\rho \approx -50\%$ ) observed at the AF–F transition in Gd<sub>3</sub>Co [1, 2], which was associated with superzone gap effects, one can suppose that the periodicity of the AF magnetic structure of the Gd<sub>3</sub>M compounds (including Gd<sub>3</sub>Rh) does not coincide with that for the crystal lattice.

The temperature dependence of the specific heat for Gd<sub>3</sub>Rh presented in figure 3 may be described considering three contributions: electronic ( $C_{el}$ ), phonon ( $C_{ph}$ ), and magnetic ( $C_m$ ). The pronounced anomaly in the  $C(T)$  curve around 112 K indicates the phase transition from the AF to the paramagnetic state with increasing temperature. Figure 4 shows the  $C/T$  versus  $T^2$  dependences in the low-temperature region that allow us to estimate the coefficient  $\gamma$  of the



**Figure 3.** (a) The temperature dependence of the specific heat of Gd<sub>3</sub>Rh. Solid curves show the nonmagnetic ( $C_{ph} + C_{el}$ ) and magnetic ( $C_m$ ) contributions. (b) The temperature dependence of the magnetic part of the entropy  $S_m$ . The vertical line indicates the Néel temperature of the compound.



**Figure 4.**  $C/T$  versus  $T^2$  dependences measured for Y<sub>3</sub>Rh (open circles) and Gd<sub>3</sub>Rh (full circles).

electronic contribution to the total specific heat for Gd<sub>3</sub>Rh as well as for its nonmagnetic partner Y<sub>3</sub>Rh. This estimation gives  $\gamma = 11 \text{ mJ mol}^{-1} \text{ K}^{-2}$  for Y<sub>3</sub>Rh and  $\gamma = 118 \text{ mJ mol}^{-1} \text{ K}^{-2}$  for Gd<sub>3</sub>Rh. Thus, as in the above-mentioned pairs of Gd<sub>3</sub>M and Y<sub>3</sub>M ( $M = \text{Co, Ni}$ ), the Gd<sub>3</sub>Rh exhibits an appreciably enhanced electronic specific heat coefficient in comparison with Y<sub>3</sub>Rh,

although these compounds have similar electronic structures according to XPS data [9]. We attribute such a great difference in  $\gamma$ -value for the  $R_3Rh$  compound depending on the type of R ion to the presence of a large contribution from spin fluctuations in the d-electron subsystem when the R ion has a nonzero magnetic moment. In our opinion, these spin fluctuations have an induced character and originate from exchange interactions between f and d electrons. In the low-temperature region an additional peak of the specific heat around 3.7 K is observed for the  $Gd_3Rh$  sample as well as for other  $Gd_3M$  compounds [2, 3]. This anomaly may be associated with the AF ordering of a small amount of  $Gd_2O_3$  [10].

In order to separate out the magnetic contribution to the total specific heat of  $Gd_3Rh$ , we have calculated the phonon contribution  $C_{ph}$  with the Debye temperature  $\Theta_D = 151$  K which was estimated using the Debye temperature  $\Theta_D = 157$  K for isostructural  $Gd_3Co$  and taking into account the difference in molar mass of these compounds. The Debye temperature for  $Gd_3Co$  was obtained by using the sound velocity and thermal expansion measurements [1]. As to the  $T$ -linear contribution to the specific heat  $C_{el} = \gamma T$ , we have taken the  $\gamma$ -value for  $Gd_3Rh$  to be equal to  $11 \text{ mJ mol}^{-1} \text{ K}^{-2}$  as for  $Y_3Rh$ , bearing in mind that the enhanced value  $\gamma = 118 \text{ mJ mol}^{-1} \text{ K}^{-2}$  originates mainly from the spin fluctuation contribution which is presumably temperature dependent. The magnetic contribution was obtained by subtraction of the nonmagnetic part:  $C_m = C_{tot} - (C_{el} + C_{ph})$ , which is shown in figure 3. As it turned out, after subtraction of electron and lattice contributions a significant specific heat remains above the ordering temperature. Bouvier *et al* [11] and Blanco *et al* [12] have shown that for Gd compounds the shape of the  $C_m(T)$  dependence below the ordering temperature as well as the magnitude of the jump in  $C_m$  at  $T = T_N$  would depend on peculiarities of the magnetic structure that appear below  $T_N$ . For the systems with equal magnetic moments, which may include F, simple AF, as well as helical and cycloidal magnetic structures, the peak height of  $C_m$  at  $T_N$  was found to be [12]

$$\Delta C_m = 5 \frac{J(J+1)}{2J^2 + 2J + 1} k_B.$$

For amplitude-modulated systems, the discontinuity in  $C_m$  at  $T_N$  is strongly reduced (to two thirds) in comparison with that for equal-moment systems. This means that specific heat data can give information on magnetic structure. From the above expression, one can find that the value of  $\Delta C_m$  for the Gd subsystem of  $Gd_3Rh$  should be equal to  $60.42 \text{ J mol}^{-1} \text{ K}^{-1}$ . Surprisingly, this value is significantly less than the value of the peak height of  $C_m$  at  $T_N$  ( $79.8 \text{ J mol}^{-1} \text{ K}^{-1}$ ) that follows from our specific heat data (see figure 3). Such a contradiction forces us to suggest the presence of an additional contribution to  $C_m$ , which is not connected with Gd magnetic moments directly. We also attribute the enhanced  $C_m$ -value around  $T_N$  for  $Gd_3Rh$  to spin fluctuations induced by the fluctuating exchange field, which acts on the itinerant d electrons of Rh from localized 4f electrons of Gd.

By integrating the  $C_m(T)/T$  dependence, we have calculated the magnetic entropy of  $Gd_3Rh$ , which is plotted in figure 3(b). As can be seen, when the temperature increases up to  $T_N = 112$  K, the magnetic part of the entropy,  $S_{mag}$ , reaches the value  $32.2 \text{ J mol}^{-1} \text{ K}^{-1}$ , which is significantly less than the theoretical value  $S_{mag}^{max} = 3R \ln(2J+1) = 3R \ln(8) = 51.86 \text{ J mol}^{-1} \text{ K}^{-1}$ . Interestingly, the ratio  $S_{mag}/S_{mag}^{max}$  at  $T_N$  for  $Gd_3Rh$  has the same value (0.62) as for  $Gd_3Co$  [2]. Since the Gd ions are not affected by the crystal field, such a discrepancy between  $S_{mag}$  and  $S_{mag}^{max}$  in  $Gd_3M$  compounds may be associated with the presence of short-range correlations between Gd magnetic moments well above the ordering temperature. In our opinion, these short-range correlations and spin fluctuations induced by f-d exchange in the d-electron subsystem are the main reason for the unusual behaviour of the electrical resistivity of  $Gd_3M$  compounds in the paramagnetic region, i.e. a pronounced

saturation effect and a temperature-independent run of the resistivity in the wide temperature interval above the ordering temperature [1, 5].

#### 4. Conclusions

The AF compound Gd<sub>3</sub>Rh exhibits a field-induced phase transition from the AF state to the field-induced parallel alignment of Gd magnetic moments below the Néel temperature  $T_N = 112$  K. The low critical transition field, which is less than in the isostructural Gd<sub>3</sub>Co [1] and Gd<sub>3</sub>Ni [7] compounds, implies a lower difference in energy of AF and F states in Gd<sub>3</sub>Rh. The observed excess of the saturation magnetic moment per Gd ion ( $\sim 0.2 \mu_B$ ) with respect to the value expected for Gd<sup>3+</sup> of  $7 \mu_B$  may be ascribed to the additional contribution from itinerant electrons associated with rhodium and the Gd 5d states. The temperature dependence of the paramagnetic susceptibility does not exactly follow the Curie–Weiss law even up to temperatures of the order  $3T_N$ . A presence of the temperature-dependent excess of the effective magnetic moment above the theoretical value  $7.94 \mu_B$  for Gd<sup>3+</sup> may result from short-range correlations in the Gd subsystem as well as from spin fluctuations in the d-electron subsystem of Rh. A giant enhancement of the coefficient  $\gamma$  of the  $T$ -linear specific heat was found to occur in Gd<sub>3</sub>Rh as well as in other Gd<sub>3</sub>M compounds (M = Co, Ni) in comparison with isostructural R<sub>3</sub>M compounds with nonmagnetic R ions (R = Y, La). We attribute the increased value of  $\gamma$  for all Gd<sub>3</sub>M compounds, about one order of magnitude larger than for Y<sub>3</sub>M and La<sub>3</sub>M, to the presence of a huge contribution from spin fluctuations induced by f–d exchange interactions in the d-electron subsystem. The giant value of this contribution originates from peculiarities of the crystal and electronic structures of R<sub>3</sub>M compounds. The peak height of the magnetic contribution,  $C_m$ , to the total specific heat at  $T_N$  in Gd<sub>3</sub>Rh was found to significantly exceed the peak value calculated within mean-field theory [12] considering the system of Gd magnetic moments only. In our opinion, the enhanced  $C_m$ -value around  $T_N$  originates also from the presence of spin fluctuations induced in the d band by the fluctuating exchange field acting from the Gd subsystem. Moreover, the magnetic contribution to the total specific heat of Gd<sub>3</sub>Rh was found to persist well above the ordering temperature. This, together with the low value of the magnetic entropy at  $T = T_N$  in comparison with the theoretical limit ( $S_m = 3R \ln(8)$ ), suggests the existence of short-range correlations as well as spin fluctuations induced by f–d exchange at  $T > T_N$ . The latter results in an additional contribution to the conduction electron scattering in Gd<sub>3</sub>M in the paramagnetic regime and causes an almost temperature-independent resistivity of these compounds over a wide temperature range above  $T_N$  [1, 2, 5].

#### Acknowledgments

We thank N V Mushnikov for his help in magnetization measurements. This work was partly supported by the grant N REC-005 of the US CRDF (Civilian Research & Development Foundation) and by the Ministry of Education of the Russian Federation (Project E00-3.4-259).

#### References

- [1] Baranov N V, Andreev A V, Kozlov A I, Kvashnin G M, Nakotte H, Aruga Katori H and Goto T 1993 *J. Alloys Compounds* **202** 215
- [2] Baranov N V, Yermakov A A, Markin P E, Possokhov U M, Michor H, Weingartner B, Hilscher G and Kotur B 2001 *J. Alloys Compounds* **329** 22



- 
- [3] Hilscher G, Michor H, Baranov N V, Markin P E and Yermakov A A 2002 Giant enhancement of the  $T$ -linear specific heat in  $R_3M$  SCES'02: *Strongly Correlated Electron System Conf. (Krakow, July 2002)* (abstracts)
  - [4] Gratz E, Hilscher G, Michor H, Markosyan A, Talik E, Czjzek G and Mexner W 1996 *Czech. J. Phys.* **46** 2031
  - [5] Talik E and Neuman M 1995 *J. Magn. Magn. Mater.* **140–144** 795
  - [6] Talik E and Neuman M 1994 *Physica B* **193** 207
  - [7] Feron J-L, Gignoux D, Lemaire R and Paccard D 1970 *Les Elements des Terres Rares* **2** 75  
Tristan N V, Nikitin S A, Palewski T, Sokolov K and Warchulska J 2002 *J. Alloys Compounds* **334** 44
  - [8] Stryjewsky E and Giordano N 1977 *Adv. Phys.* **26** 487
  - [9] Talik E, Neuman M, Slebarski A and Winiarski A 1995 *Physica B* **212** 25
  - [10] Miller A E, Jelinek F J, Gschneidner K A Jr and Gerstein B C 1971 *J. Chem. Phys.* **55** 2645
  - [11] Bouvier M, Lethuillier P and Schmitt D 1991 *Phys. Rev. B* **43** 13137
  - [12] Blanco J A, Gignoux D and Schmitt D 1991 *Phys. Rev. B* **43** 13145