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Extra T -linear specific heat contribution induced by the f–d-exchange in Gd–Ni binary compounds

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Abstract

Specific heat measurements performed for Gd–Ni binary compounds with 1:2, 1:1 and 3:1 stoichiometry have revealed an additional contribution to the coefficient γ of the T -linear term of the low-temperature specific heat in comparison with that obtained for isostructural paramagnetic counterparts R–Ni (R = Y, Lu, La). This extra contribution $\Delta\gamma$ is found to grow linearly with increasing Gd concentration from nearly zero for GdNi₅ up to $\Delta\gamma \approx 21.5 \text{ mJ g-at.}^{-1} \text{ K}^{-2}$ for Gd₃Ni. To explain the appearance of $\Delta\gamma$ and its dependence on the strength of the f–d exchange interaction in Gd-rich binary compounds with Ni a new mechanism enhancing the effective mass of conduction electrons is suggested. The increased γ value in Gd-containing compounds is attributed to spin fluctuations induced by the f–d exchange interaction in the hybridized 3d–5d electron subsystem.

1. Introduction

The magnetic ordering in rare earth (R)–3d transition metal (T) compounds is considered to result from several exchange interactions [1–4]. First, there is the intra-atomic 4f–5d exchange in rare earth ions with a non-filled 4f electron shell, which leads to the polarization of 5d spin moments parallel to 4f moments. The existence of such a magnetic polarization of the 5d electron shell in the R–T compounds was revealed by different experimental methods [5]. The energy of the 4f–5d exchange decreases with growing rare-earth atomic number owing to the contraction of the 4f shell and reduction of the overlap between the 4f and 5d electron densities. The next mechanism is the f–d exchange interaction which leads to the antiparallel alignment of the 4f and 3d spins due to the short-range exchange and hybridization effects between the 5d and 3d electrons. The R–R exchange is usually weakest in the R–T intermetallics. According to the model which is introduced by Campbell [1] and accepted at present in the literature, the indirect 4f–4f coupling in pure

rare earths is provided by the intra-atomic 4f–5d exchange and inter-atomic 5d–5d interaction between the spin polarized 5d electrons of neighboring R atoms. In the R_nT_m binary compounds with high rare earth content ($n:m = 1:1, 3:1$), such a type of exchange interaction may apparently exist together with a 4f–5d–3d–5d–4f mechanism. Depending on the $n:m$ ratio the exchange interaction, either in the rare earth or transition metal sublattice, is a driving force leading to magnetic order. In the 3d metal rich R_nT_m compounds with large 3d–3d exchange, the T moment exists independently from the magnetic state of the R sublattice. The hybridization between 3d and 5d electrons results in the presence of negative 5d moments. The alignment of the 4f moments parallel to the 5d moments appears as a result of the 4f–5d intra-atomic interactions. At high R concentrations the exchange interaction within 3d electron subsystem is not enough to produce a 3d band splitting. The exchange field acting from the 4f moments may induce negative moments or/and spin fluctuations in the 3d electron subsystem via 4f–5d and 5d–3d exchange interactions together with 5d–3d hybridization.

A decrease of the T-magnetic moment with rising $n:m$ ratio was explained in earlier works [6–8] as the gradual filling of the T 3d band by outer-shell electrons of R atoms. Within the R–Co series, the magnetic moment per Co atom is found to disappear when the R atomic concentration exceeds 1/3. The Co 3d subsystem in the boundary RCO_2 compounds exhibits an instability and itinerant electron metamagnetism [6]. In RCO_2 compounds with R ions having localized magnetic moments (except $\text{R} = \text{Tm}$), the moment on the cobalt sites ranges from 0.7 up to $1.0 \mu_B$, while YCo_2 and LuCo_2 with non-magnetic yttrium and lutetium are spin-fluctuating Pauli paramagnets (itinerant metamagnets). Because of the instability of the Co-magnetic moments the properties of RCO_2 are observed to be strongly influenced by spin fluctuations [6]. According to the charge-transfer model the magnetic moment per Ni atom should disappear in R–Ni binaries when the R concentration exceeds 1/6. The YNi_5 compound is, indeed, found to be a Pauli-type paramagnet [9]. However, an induced magnetic moment of about $0.16 \mu_B$ is observed on Ni atoms in GdNi_5 [10]. A further increase of the R content above 1/6 is accompanied by a 3d band splitting in Y_2Ni_7 [11] and YNi_3 [12]. The very weak itinerant ferromagnetism of Y_2Ni_7 and YNi_3 is ascribed to the fine structure of the electronic density of states (DOS) in the region of the Ni 3d–Y 4d (5d in rare earths) hybridized states. In the compounds with higher R concentrations (RNi_2 , RNi , R_3Ni), the Ni moment was accepted to be zero. However, magnetic circular dichroism (MCD) experiments [13] and magnetic Compton profile measurements [14] performed recently for GdNi_2 have shown that the Ni 3d band in this compound is not fully occupied and the Ni atoms exhibit a magnetic moment of about $0.2 \mu_B$. The presence of a magnetic moment on the Ni atoms $\sim 0.1 \mu_B$ has been revealed by soft x-ray absorption spectra and MCD measurements even for the equiatomic GdNi [15]. In all these cases, the magnetic moment induced on the Ni atoms was found to be antiparallel to the Gd-magnetic moment as in other R_nT_m intermetallics with heavy rare earths. Bearing in mind the presence of this Ni induced moment one can suggest that the Ni 3d electrons are involved in the exchange interactions and affect the physical properties of the R rich R–Ni compounds despite the absence or low value of the magnetic moment on the Ni atoms.

The present work focuses on a specific heat study of some Gd_nNi_m compounds and their paramagnetic counterparts R_nNi_m in which R ions (Y, La, Lu) do not exhibit magnetic 4f moments. The specific heat data are analyzed as a function of the Gd concentration in order to obtain additional information on the magnetic state of Ni 3d electrons in R–Ni compounds and to achieve a better understanding of mechanisms responsible for electron mass enhancement in metallic magnets.

2. Experimental details

The GdNi_2 compound was prepared by inductive levitation melting using rare earth metals and yttrium of 99.9% purity, and Ni of 99.99% purity, respectively. A 0.96:2 stoichiometry was used to prevent the formation of foreign phases since

according to previous investigations [16] the single-phase RNi_2 samples can be obtained with R deficiency. Samples were sealed in an evacuated quartz tube and homogenized at 800°C for 2 weeks. In order to compare the specific heat of GdNi_2 with its paramagnetic analog and to evaluate correctly the lattice contribution to the total specific heat we prepared, using the above-mentioned conditions, the isostructural $\text{Lu}_{0.794}\text{Y}_{0.206}\text{Ni}_2$ compound with the same molar mass [17]. The x-ray diffraction measurements have been performed on a Bruker D8 diffractometer, with $\text{Cu K}\alpha$ radiation at room temperature. The crystal structure of the samples was identified by x-ray diffraction as a superstructure of the cubic Laves structure C15. The lattice parameter a was obtained as 14.390 and 14.198 \AA for GdNi_2 and $\text{Lu}_{0.794}\text{Y}_{0.206}\text{Ni}_2$ respectively. Our data for GdNi_2 are in good agreement with measurements reported in [16]. The RNi samples with $\text{R} = \text{Gd, La, Lu}$ were obtained by melting in an arc oven. The ingots were melted several times to ensure homogeneity. The samples thus obtained were annealed at 650°C for one week. From the absence of observed external lines, the GdNi sample was determined to be CrB-type single phase with lattice parameters: $a = 3.767 \text{ \AA}$, $b = 10.306 \text{ \AA}$ and $c = 4.239 \text{ \AA}$. The lattice parameters for LaNi having the CrB-type structure were determined as: $a = 3.914 \text{ \AA}$, $b = 10.754 \text{ \AA}$ and $c = 4.376 \text{ \AA}$. The LuNi sample was confirmed to be of the FeB-type structure with $a = 6.884 \text{ \AA}$, $b = 4.076 \text{ \AA}$, $c = 5.375 \text{ \AA}$. The lattice parameters for our RNi samples compare well with the reported values [9, 18]. The Gd_3Ni and Y_3Ni were also melted in an arc oven. According to x-ray diffraction analysis the Gd_3Ni and Y_3Ni compounds exhibit an orthorhombic crystal structure of the Fe_3C type [19] with the lattice parameters $a = 6.939 \text{ \AA}$, $b = 9.670 \text{ \AA}$, $c = 6.336 \text{ \AA}$ and $a = 6.924 \text{ \AA}$, $b = 9.661 \text{ \AA}$, $c = 6.348 \text{ \AA}$ respectively. It should be noted, that some traces of foreign phases (less than 3%) were revealed by a metallographic analysis in all samples, even in the case of an absence of extra lines on powder diffraction patterns.

Specific heat measurements for the R_3Ni and RNi were made by an adiabatic step-heating technique in TU Vienna on samples with a typical mass of 500 mg. 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 NBS copper standard. The accuracy of the experiment was better than 1% below 100 K and 1–3% above. For the RNi_2 compounds, the specific heat measurements were performed using a Quantum Design PPMS-6000 system.

3. Results

3.1. Gd_3Ni

The Gd_3Ni compound having the highest Gd concentration within Gd–Ni intermetallics enters an antiferromagnetic (AF) order below the Neel temperature $T_N \sim 96 \text{ K}$. As it is seen from figure 1(a), the phase transition at $T = T_N$ is accompanied by a pronounced λ -type anomaly. This critical temperature is very consistent with the $T_N \sim 97\text{--}100 \text{ K}$,

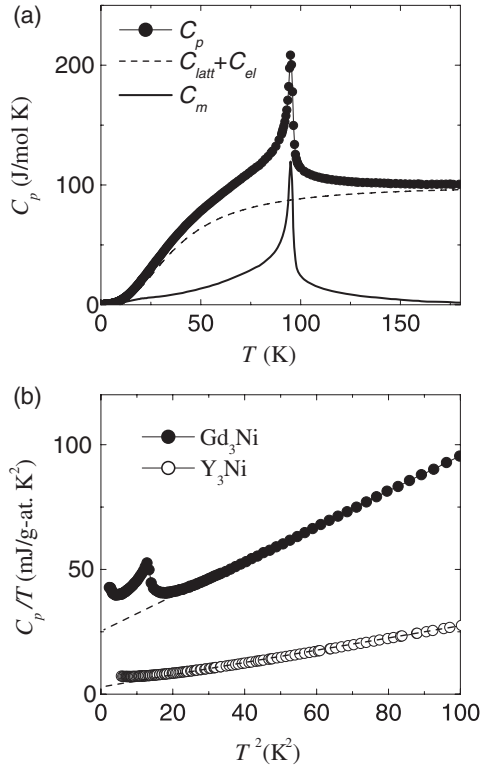


Figure 1. (a) The temperature dependence of the specific heat of Gd_3Ni . Dashed and solid curves show the non-magnetic ($C_{\text{ph}} + C_{\text{el}}$) and magnetic (C_{m}) contributions respectively. (b) C_p/T versus T^2 dependences measured for Gd_3Ni (full circles) and Y_3Ni (open circles).

obtained previously [20]. In order to separate the magnetic and phonon contribution to the heat capacity of Gd_3Ni we used a Debye function with $\Theta_{\text{D}} = 157$ K obtained by sound velocity and thermal expansion measurements performed for the isostructural Gd_3Co compound [21] having nearly the same molar mass. Usually, in order to calculate the lattice contribution $C_{\text{latt}}(T)$ to the total specific heat one uses the data of a non-magnetic isostructural analog. The data are then compared by assuming a correction to the Debye temperature, which takes into account the difference in the mass of the average atom as well as the difference in the strength of an inter-atomic binding force. In a simplified model, the Debye temperature is proportional to $(K/m)^{1/2}$ [22], where K is the spring constant and m is the mass of the average atom, i.e. the molar mass.

From the low-temperature part of the C_p/T versus T^2 dependence presented in figure 1(b) for the paramagnetic Y_3Ni compound we obtained the Θ_{D} value to be equal to 206 K, which is slightly less than 215 K derived in [23] from low-temperature specific heat data. The estimation of the Debye temperature for Gd_3Ni using $\Theta_{\text{D}} = 206$ K for Y_3Ni and the expression:

$$\frac{\Theta_{\text{D}}(\text{Gd}_3\text{Ni})}{\Theta_{\text{D}}(\text{Y}_3\text{Ni})} = \left[\left(\frac{m_{\text{Y}_3\text{Ni}}}{m_{\text{Gd}_3\text{Ni}}} \right) \cdot \left(\frac{v_{\text{Y}_3\text{Ni}}}{v_{\text{Gd}_3\text{Ni}}} \right)^{1/3} \right]^{1/2} \quad (1)$$

gives $\Theta_{\text{D}}(\text{Gd}_3\text{Ni}) = 161$ K. Here we assumed (as a rough approximation) that the binding forces vary as $K \propto (v)^{-1/3}$

within R_3Ni series (v denotes the unit cell volume). If we take $\Theta_{\text{D}} = 150.5 \pm 5$ K [24] and lattice parameters [9] for the isostructural compound La_3Ni , such an estimate leads us to the value $\Theta_{\text{D}} = 146 \pm 5$ for Gd_3Ni . Thus, our value $\Theta_{\text{D}} = 157$ K which we used for the calculation of the lattice contribution to the total specific heat of Gd_3Ni lies between those estimated from specific heat data for Y_3Ni and La_3Ni as the reference materials and seems to be quite reasonable.

The solid and dashed lines in figure 1(a) represent the magnetic specific heat contribution, C_{m} , and the non-magnetic one, $C_{\text{ph}} + C_{\text{el}}$, respectively. For the electronic contribution $C_{\text{el}} = \gamma T$ we used the value $\gamma = 14$ $\text{mJ mol}^{-1} \text{K}^{-2}$ for Y_3Ni obtained from data presented in figure 1(b). This γ value agrees with those reported for this compound in [23] ($\gamma = 15$ $\text{mJ mol}^{-1} \text{K}^{-2}$) and in [25] ($\gamma = 14$ $\text{mJ mol}^{-1} \text{K}^{-2}$). Two peculiarities of the $C_{\text{m}}(T)$ should be mentioned: (i) persistence of the magnetic contribution to the specific heat of Gd_3Ni in a wide temperature range above the magnetic ordering temperature, and (ii) an enhanced value of the peak height of the C_{m} at T_{N} . The integral of $C_{\text{m}}(T)/T$ over temperature yields the magnetic entropy gain, S_{mag} , which for Gd_3Ni is about 32 $\text{J mol}^{-1} \text{K}^{-1}$ at T_{N} being significantly less than the value expected, $S_{\text{mag}}^{\text{max}} = 3R \ln(2J + 1) = 51.86$ $\text{J mol}^{-1} \text{K}^{-1}$. Nearly the same ratio $S_{\text{m}}/S_{\text{m}}^{\text{max}} \approx 0.62$ was also observed for other Gd_3T ($\text{T} = \text{Co}$ [26], Rh [27]). A lower S_{m} value at $T = T_{\text{N}}$ for Gd_3Ni in comparison with the theoretical one is also reported in [23]. Bearing in mind that the Gd ions are not affected by the crystal field because of zero orbital moment, such a discrepancy between $S_{\text{mag}}(T = T_{\text{N}})$ and $S_{\text{mag}}^{\text{max}}$ in Gd_3T compounds may be associated with the presence of short-range correlations between Gd-magnetic moments well above the ordering temperature. The value of the C_{m} peak height at $T = T_{\text{N}}$, ΔC_{m} , for magnetically ordered systems with equal magnetic moments is given by [28]:

$$\Delta C_{\text{m}} = 5 \frac{J(J+1)}{2J^2 + 2J + 1} k_{\text{B}}. \quad (2)$$

Suggesting that only Gd ions have magnetic moments, the height of the magnetic anomaly ΔC_{m} can readily be derived from equation (2): $\Delta C_{\text{m}} \sim 60.5$ $\text{J mol}^{-1} \text{K}^{-1}$. However, as follows from our experimental specific heat data (see figure 1(a)), the $\Delta C_{\text{m}}(T = T_{\text{C}}) \sim 119.6$ $\text{J mol}^{-1} \text{K}^{-1}$, which is significantly higher than the expected value. Such deviations are indicative of the presence of an additional contribution to C_{m} , which is not directly associated with Gd moments.

Together with the data for Y_3Ni , figure 1(b) shows the C_p/T versus T^2 dependence for Gd_3Ni in the low-temperature region. An anomaly of the specific heat observed on Gd_3Ni at $T \sim 3\text{--}4$ K is attributed to the antiferromagnetic ordering of a small amount of Gd_2O_3 [29]. For Gd_3Ni , the extrapolation of C_p/T versus T^2 dependence from the temperature interval above 5 K to $T = 0$ gives a significantly enhanced γ value ~ 25 $\text{mJ g-at.}^{-1} \text{K}^{-2}$ in comparison with $\gamma = 3.5$ $\text{mJ g-at.}^{-1} \text{K}^{-2}$ for Y_3Ni . A contribution of the insulating oxide impurity Gd_2O_3 phase to γ can be rather safely excluded. We used the unit ($\text{mJ g-at.}^{-1} \text{K}^{-2}$) for γ in order to compare the results obtained for compounds with different numbers of atoms per formula unit. The enhancement

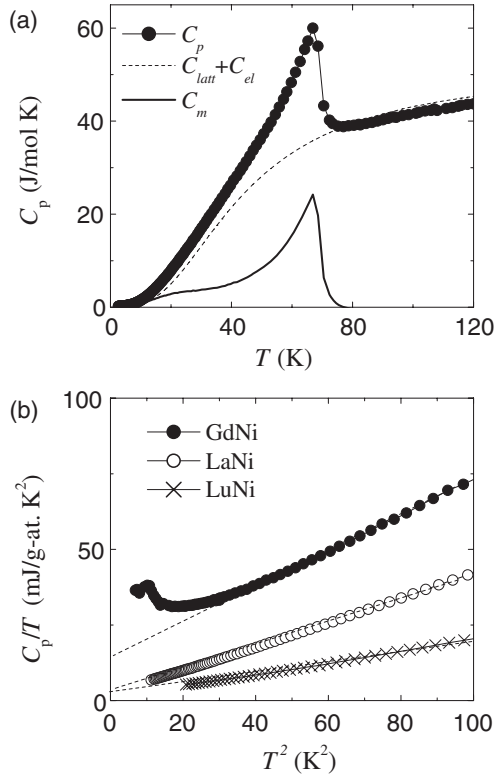


Figure 2. (a) The temperature dependence of the specific heat of GdNi. Dashed and solid curves show the non-magnetic ($C_{ph} + C_{el}$) and magnetic (C_m) contributions respectively. (b) C_p/T versus T^2 dependences measured for GdNi (full circles) and non-magnetic compounds LaNi (open circles) and LuNi (crosses).

of γ of Gd₃Ni as compared to Y₃Ni appears despite of the close similarity of the electronic structure of both compounds which is indicated by x-ray photoelectron spectroscopy data [30].

3.2. GdNi

The magnetic ground state of the GdNi compound was classified as a simple ferromagnetic one up to the recent time since the Ni-magnetic moment was accepted to be zero. However, according to the recent MCD experiments GdNi has a ferrimagnetic order [15], since Ni is found to retain a magnetic moment of about 0.1 μ_B /atom, coupled antiparallel to the Gd moment, as in other heavy rare earth–transition metal compounds.

As can be seen from figure 2(a), the ferrimagnetic order in GdNi is accompanied by a λ -type anomaly at $T_C \approx 68$ K, being in agreement with that published in [31]. We have also measured the specific heat of paramagnetic compounds LaNi and LuNi as reference materials. For the estimation of the lattice contribution to the specific heat of GdNi we used the $C_p(T)$ data for LaNi. From C_p/T versus T^2 dependence for LaNi displayed in figure 2(b), the Θ_D value was estimated to be equal to 169 K. Then by using this value and applying the expression (1) for the $\Theta_D(\text{GdNi})/\Theta_D(\text{LaNi})$ ratio, we found $\Theta_D = 165$ K for GdNi. The electronic contribution C_{el} was calculated with $\gamma = 3.8$ mJ mol⁻¹ K⁻² for LaNi taken from

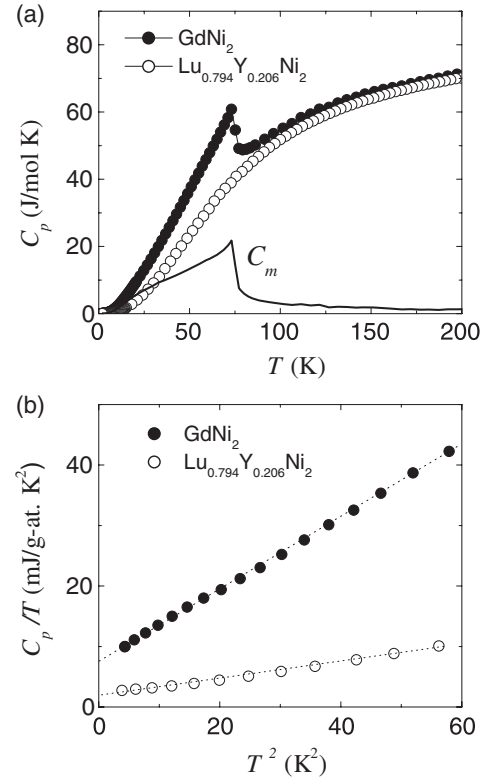


Figure 3. (a) The temperature dependence of the specific heat for GdNi₂ (full circles) and its non-magnetic partner Lu_{0.794}Y_{0.206}Ni₂ (open circles). Solid curve shows the magnetic (C_m) contribution. (b) C_p/T versus T^2 dependences for GdNi₂ (full circles) and Lu_{0.794}Y_{0.206}Ni₂ (open circles).

data presented in figure 2(b). After subtraction of the non-magnetic part ($C_{ph} + C_{el}$) from the total specific heat of GdNi we obtained the magnetic contribution C_m shown in figure 2(a) by a solid line. The C_m peak height at $T = T_C$ is also observed to be enhanced, $C_m \sim 24.2$ J mol⁻¹ K⁻¹ in comparison with 20.15 J mol⁻¹ K⁻¹ calculated using equation (2). It should be noted that the enlarged $C_m(T = T_C)$ values ~ 27 for GdNi [31], 22 and 24 J mol⁻¹ K⁻¹ for GdNi_{1-x}Cu_x compounds with $x = 0$ and $x = 0.3$ [32] were also observed. The coefficient γ of the T -linear specific heat ~ 15 mJ g-at.⁻¹ K⁻² for GdNi substantially surpasses the γ value for LaNi and LuNi compounds $\gamma \sim 1.9$ mJ g-at.⁻¹ K⁻² (see figure 2(b)). A peak of the specific heat observed on GdNi at $T \sim 3$ –4 K originates in the presence of a small amount of monoclinic Gd₂O₃ [29] as in Gd₃Ni. Our γ values for paramagnetic RNi compounds are in agreement with data published in literature (2.5 mJ g-at.⁻¹ K⁻² for LaNi [33] and 1.35 mJ g-at.⁻¹ K⁻² for LuNi [34]).

3.3. GdNi₂

Figure 3 shows our specific heat data obtained for GdNi₂ and for its paramagnetic counterpart Lu_{0.794}Y_{0.206}Ni₂ with the same molar mass. We only briefly describe the results displayed since the specific heat behavior of these compounds was characterized in detail in a previous work [17].

Table 1. The coefficient γ of the T -linear term of the total specific heat of R–Ni compounds with R = Gd, Y, Lu, La. The γ values for pure Gd, Y and Lu are presented for comparison.

Compound	γ (mJ g-at. ⁻¹ K ⁻²)		
	R = Gd	(R = Y, La, Lu)	
R	6.38 [41]	8.194 (Lu) [41]	7.878 (Y) [41]
R ₃ Ni	25 Present work	3.5 (Y) Present work	3.5 (Y) [25]
RNi	15 Present work	3.75 (Y) [23]	1.9 (Lu) Present work
		1.9 (La) Present work	1.9 (La) [33]
		2.5 (La) [34]	1.35 (Lu) Present work
		1.7 (Lu) Present work	1.7 (Lu) [36]
RNi ₂	7.3 Present work 8.83 [36]	1.7 (Lu _{0.794} Y _{0.206}) Present work	2.0 (Y) [36]
		2.2 (Lu) [38]	1.7 (Y) [39]
		2.1 (Lu) [40]	6.06 (Y) [43]
		6.06 (Y) [43]	6.08 (La) [43]
		6.08 (La) [43]	
RNi ₅	6.0 [42]		

A ferrimagnetic structure with antiparallel alignment of Gd moments and magnetic moments induced on Ni atoms (see above) appears in this compound below $T_C \approx 75$ K. The specific heat anomaly at this temperature is very consistent with previous studies [35–37]. As shown in [17] and [38], the $C_p(T)$ dependence of RNi₂ compounds (R = Lu, Gd) can not be satisfactorily described by a simple Debye model with a constant value of the Debye temperature. Therefore, the $C_p(T)$ data of the paramagnetic Lu_{0.794}Y_{0.206}Ni₂ compound, having the same molar mass as GdNi₂, were used to obtain the magnetic contribution C_m from the total specific heat of GdNi₂ [17]. As follows from figure 3, the observed specific heat of the RNi₂ compounds has similar peculiarities as the above considered R–Ni binaries. First, the C_m peak height 21.8 J mol⁻¹ K⁻¹ at $T = T_C$ for GdNi₂ slightly exceeds the theoretical limit 20.15 J mol⁻¹ K⁻¹. Secondly, as obvious from figure 3(b), GdNi₂ exhibits an enhanced γ -value as compared to Lu_{0.794}Y_{0.206}Ni₂ (7.3 mJ g-at.⁻¹ K⁻² and 1.7 mJ g-at.⁻¹ K⁻², respectively). The latter value agrees well with 1.7 mJ g-at.⁻¹ K⁻² for YNi₂ [39] and 2.1 mJ g-at.⁻¹ K⁻² for LuNi₂ [40]. It should be noted, that our present results are in good agreement with the specific heat measurements of Gd_{1-x}Y_xNi₂ pseudobinaries performed earlier [36]. As is shown in [36], the GdNi₂ compound exhibits a substantially larger value of γ (8.83 ± 0.09 mJ g-at.⁻¹ K⁻²) than YNi₂ ($\gamma = 2.0$ mJ g-at.⁻¹ K⁻²).

4. Discussion

The γ values obtained in the present work for the R–Ni compounds with R = Gd, Y, La, Lu are displayed in table 1. We also added the data existing in literature for these R–Ni binaries together with γ values derived from the specific heat measurements for electrotransport-purified Gd, Lu, and Y [41]. The electronic specific heat coefficients for Gd, Lu and Y seem to be quite close to each other [41].

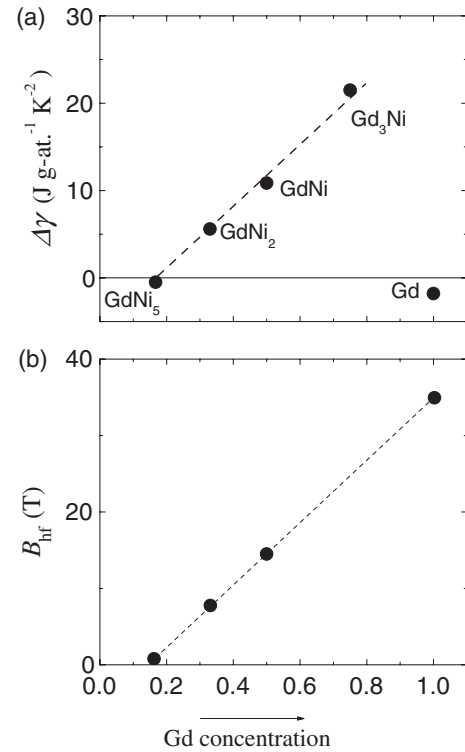


Figure 4. (a) The difference $\Delta\gamma$ between the γ values for Gd-containing R–Ni compounds and their non-magnetic analogs as a function of R concentration. (b) The variation of the hyperfine field B_{hf} on Gd sites in the GdNi₅, GdNi₂, GdNi, Gd series according to [44].

This means that the presence of the ferromagnetic order in Gd does not significantly affect the γ value in comparison with that observed for non-magnetic Lu and Y. This also holds for the two isostructural compounds GdNi₅ and YNi₅ as well. According to the specific heat data presented in [42] the magnetically ordered GdNi₅ exhibits nearly the same γ value (6 ± 0.5 mJ g-at.⁻¹ K⁻²) as the paramagnetic compounds YNi₅ (6.06 mJ g-at.⁻¹ K⁻² [43]) and LaNi₅ (6.08 mJ g-at.⁻¹ K⁻² [43]). However, it is not the case for other R–Ni binaries with higher R concentration. In figure 4(a) we plotted the difference $\Delta\gamma$ between the γ values for Gd-containing R–Ni compounds and their non-magnetic analogs as a function of R concentration. The difference $\Delta\gamma$ increases linearly with increasing R content from nearly zero for RNi₅ up to a value $\Delta\gamma = \gamma(\text{Gd}_3\text{Ni}) - \gamma(\text{Y}_3\text{Ni}) \approx 21.5$ mJ g-at.⁻¹ K⁻². Note that the difference ΔC_m between the experimental value of the C_m peak height at $T = T_C(T_N)$ and the value calculated using equation (2) shows a concentration dependence as well, it increases with growing Gd concentration ($\Delta C_m \sim 1.7$ J mol⁻¹ K⁻¹; 4.1 J mol⁻¹ K⁻¹ and 59.1 J mol⁻¹ K⁻¹ for GdNi₂, GdNi and Gd₃Ni, respectively). It is worth mentioning that the presence of an additional contribution to the T -linear term of the specific heat is also revealed for Gd₃Co [26] and Gd₃Rh [27] compounds. Their coefficient $\gamma = 27.5$ –30 mJ g-at.⁻¹ K⁻² is enhanced by one order of magnitude as compared to the paramagnetic compounds Y₃Co (3.75 mJ g-at.⁻¹ K⁻² [26]) and Y₃Rh (2.75 mJ g-at.⁻¹ K⁻² [27]).

The investigation of the magnetic and thermal properties of Pd₂RIn compounds with R = Gd, Lu, La [45] have shown that the magnetic contribution, S_m , to the total entropy of Gd-containing compound Pd₂GdIn substantially exceeds (by about 40%) the expected value. The increased S_m value in Pd₂GdIn was explained by the presence of a huge additional contribution to the T -linear specific heat in comparison with paramagnetic Pd₂LuIn and Pd₂LaIn compounds. The γ value for the Pd₂GdIn was estimated to be about 202 mJ mol⁻¹ K⁻², while a significantly lower coefficient γ was observed for paramagnetic Pd₂LaIn and Pd₂LuIn (4.0 ± 0.5 mJ mol⁻¹ K⁻² and 10 ± 1 mJ mol⁻¹ K⁻², respectively [45]). The enhanced γ coefficient obtained for Gd-containing intermetallic compounds with d-transition metals cannot be ascribed to the contribution of 4f electron states to the DOS at the Fermi level. The 4f shell of Gd is half filled and consequently particularly stable. The Gd 4f states are located far below E_f . There are several mechanisms that may be considered as origins of additional contributions to the T -linear term of the total specific heat of magnetically ordered metallic compounds: (a) the electron–phonon mass enhancement; (b) the change in the DOS near E_f due to the d-band splitting originating from magnetic ordering; (c) the electron-magnon enhancement; and (d) the contribution from spin fluctuations.

As to the electron–phonon enhancement effects, they should be similar for the magnetic and non-magnetic R_nNi_m pairs because of identical crystal structure. Very low values or an absence of a magnetic moment observed on Ni atoms in the GdNi₅, GdNi₂, GdNi and Gd₃Ni implies only a weak change of DOS at E_f through the magnetic transition in these compounds. The proximity of the γ values for pure Gd, Y and Lu (see table 1) shows that the electron-magnon interaction cannot be considered as a main factor determining the enhancement of the γ observed for the Gd–Ni compounds with high Gd concentrations. For pure rare earths, the different mechanisms responsible for the mass enhancement of conduction electrons are considered theoretically [46, 47]. However, these theories cannot explain the results obtained in our work for R–Ni compounds. As can be seen from figure 4, starting from pure Gd the large extra contribution to the T -linear specific heat appears if the Ni atoms with unfilled 3d electron states are introduced to the Gd-based compound. Therefore, one can suggest that $\Delta\gamma$ appears due to the interactions in which these 3d electrons of Ni are involved. A number of nearly ferromagnetic or antiferromagnetic compounds based on transition metals is observed to exhibit an enhanced electronic specific heat coefficient (see [48], for overview). Such a behavior is associated with spin fluctuations in the itinerant electron subsystem. The paramagnetic RNi₂, RNi and R₃Ni compounds (R = Y, La, Lu) can hardly be considered as systems which are strongly influenced by spin fluctuations, because their γ values are substantially lower than those of usual systems exhibiting a spin-fluctuation behavior. Typical values of spin-fluctuating compounds YCo₂ and LuCo₂ are about 4–5 times higher (~ 11.3 – 12.3 mJ g-at.⁻¹ K⁻² for YCo₂ [49, 50] and $\gamma \sim 8.9$ mJ g-at.⁻¹ K⁻² for LuCo₂ [51]) than for YNi₂ and

LuNi₂ (see table 1). This is because of the lower values of DOS at the Fermi level and the Stoner enhancement factor in RNi₂ as compared to RCo₂ compounds [6]. As to the Gd–Ni compounds, the additional spin-fluctuation contribution is suggested as being induced by the exchange interactions originating from the Gd sublattice.

It is worth mentioning that for the Gd–Ni binary compounds, the hyperfine fields, B_{hf} , on Gd sites are obtained by using the perturbed angular correlation measurements on the nuclei of closed-shell ¹¹¹Cd probe atoms [45]. Figure 4(b) shows the change of B_{hf} values within the GdNi₅, GdNi₂, GdNi, Gd series. As can be seen, the hyperfine field shows a linear growth when going from the GdNi₅ to pure Gd. Since ¹¹¹Cd has a closed electron shell, the value of the magnetic hyperfine field is associated with the Fermi contact term in the magnetic nucleus–electron interaction and reflects the spin polarization of the conduction electrons. The magnetic order in Gd–Ni compounds is sustained by indirect 4f–4f coupling via the above-mentioned 4f–5d–3d–5d–4f path. The s conduction electrons are spin polarized by the interaction with the hybridized 3d–5d electrons [2]. The growth of B_{hf} with increasing Gd content in the Gd–Ni compounds apparently results from shortening of the Gd–Gd distances and from increasing 5d–5d and 5d–3d short-range interactions. The pronounced correlation between the evolution of the additional contribution $\Delta\gamma$ and the hyperfine field B_{hf} on Gd sites within the binary Gd–Ni compounds thus suggests that the presence of $\Delta\gamma$ and its concentration dependence is associated with the additional contribution from spin fluctuations induced by the f–d exchange in the 3d electron subsystem hybridized with 5d electrons of Gd. The growth of $\Delta\gamma$ and the reduction of the 3d electron concentration with increasing R content in R–Ni binaries may appear contradictory. However, one should take into account that according to numerous investigations of the R–T intermetallics (see [5], for instance) the strength of the f–d exchange increases with increasing R content. Moreover, f–d exchange-induced spin fluctuations also involve the 5d electrons of Gd via the 5d–3d coupling. The concentration of these 5d electrons participating in the 5d–3d exchange increases with increasing Gd content in the Gd–Ni series.

5. Conclusion

The study of the specific heat of GdNi₂, GdNi and Gd₃Ni compounds and their non-magnetic counterparts revealed a significantly enhanced coefficient γ of the T -linear contribution to the total specific heat of the Gd-containing compounds. The extra contribution $\Delta\gamma$ is found to increase from nearly zero for GdNi₅ [42, 43] up to $\Delta\gamma = 21.5$ mJ g-at.⁻¹ K⁻² for Gd₃Ni. The fact that the enhanced γ value is observed in the Gd-rich compounds with d-transition metals (Ni in our case) suggests that this extra contribution results from spin fluctuations induced by the f–d exchange in the 3d–5d hybridized electron subsystem. The linear growth of $\Delta\gamma$ with increasing Gd concentration in the GdNi₅, GdNi₂, GdNi and Gd₃Ni series is found to correlate with the increase of the magnetic hyperfine field on Gd sites [44], which further supports the fluctuation induced nature of $\Delta\gamma$. The enhanced

magnetic specific heat observed around the magnetic ordering temperatures in GdNi₂, GdNi and Gd₃Ni apparently has the same origin. It results from spin fluctuations induced by the fluctuating exchange field, which acts on the hybridized 3d and 5d electrons from localized 4f electrons of Gd. The difference ΔC_m between experimental and calculated maximal values of C_m increases when going from GdNi₂ to Gd₃Ni, i.e. with increasing f–d exchange. The presence of the additional contribution to the T -linear specific heat arising from the f–d exchange-induced spin fluctuations is a rather general phenomenon. This mechanism is not explained by existing theories. Such a kind of mass enhancement of the conduction electrons may take place in other rare earth–transition metal compounds in which the d-band of the transition element is not fully occupied and the d–d exchange interaction alone is not enough to produce the d-band splitting.

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