Enhanced magnetic entropy in GdNi$_2$

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Measurements of the specific heat have been performed on Gd$_{1-x}$Y$_x$Ni$_2$ ($x=0,0.2$) compounds and their nonmagnetic analogs Lu$_{1-y}$Y$_y$Ni$_2$, which have similar molar masses. It is found that the difference between the entropies of magnetic and nonmagnetic compounds with identical molar masses surpasses substantially (by 14-19%) the theoretical limit for the magnetic contribution $S_m = (1-x)R\ln(8)$ calculated assuming that only Gd ions possess a magnetic moment. This observed enhancement of the magnetic entropy in Gd$_{1-x}$Y$_x$Ni$_2$ is believed to result from spin fluctuations induced by f-d exchange in the $3d$ electron subsystem of Ni.

A well known observation for rare earth (R)–$3d$ transition-metal (T) binary-intermetallic compounds is the reduction of the magnetic moment per $3d$ metal atom (M_T) with increasing rare earth content.[1] For example, the magnetic moment per Co atom is found to disappear when the R concentration exceeds $1/3$. The Co $3d$ subsystem in the boundary RCo$_2$ compounds reveals an instability and itinerant metamagnetism.[2] For the R-Ni series, the Ni magnetic moment is observed to vanish even for RNi$_5$ compounds, while a reappearance of the $3d$ band splitting was found upon further increase of the R content [Y$_2$Ni$_7$ and YNi$_3$ (Ref. 1)]. Until recently, the Ni magnetic moment in compounds with higher R concentration (RNi$_2$, RNi, R_3Ni) was taken to be zero. The evolution of the M_T value in R-T intermetallic compounds was explained by a gradual filling of the T $3d$ band by outer-shell electrons of R atoms.[2,3] However, recent x-ray magnetic circular dichroism[4] (MCD) and magnetic Compton profile[5] experiments have shown that the Ni $3d$ band in GdNi$_2$ is not fully occupied and the Ni atoms exhibit a magnetic moment of about $(0.2-0.23)\mu_B$. These results are in agreement with bulk magnetization measurements.[6] The presence of a magnetic moment on Ni atoms up to $\sim 0.1\mu_B$ was revealed by MCD measurements even for GdNi.[7] In all these cases the Ni magnetic moment was found to be antiparallel to the Gd magnetic moment, as in other R-T intermetallics with heavy rare earths. For compounds with a high R content, such as GdNi (Ref. 8) and Gd$_3$Ni (Ref. 9) the values of the effective magnetic moment per Gd ion were found to be enhanced in comparison with the μ_{eff} value of the free Gd^{3+} ion.

In the present work we have investigated the specific heat and entropy content of the GdNi$_2$ compound. Due to potential applications for magnetic cooling,[10,11] the attention on specific heat and magnetocaloric effect studies has recently substantially increased.

According to previous investigations of the crystal structure of RNi$_2$,[12] which show that single-phase samples can be obtained with some R deficiency, we have prepared several GdNi$_2$ samples with various deviations from the 1:2 stoichiometry (0.96:2; 0.98:2, and 1:2). All compounds were prepared by melting in levitation in an argon atmosphere. The

ingots obtained were annealed at 800 °C for 2 weeks. X-ray diffraction and metallographic analysis were used to examine the phase purity of the compounds. The best result was obtained for the compound with 0.96:2 stoichiometry, in agreement with the data of Lindbaum *et al.*[12] The crystal structure of the sample was identified as a superstructure of the cubic Laves structure $(C15)$.[12] Usually, in order to calculate the lattice contribution $C_{latt}(T)$ to the total specific heat one uses the data of a nonmagnetic isostructural analog. The data are then compared by assuming a correction to the Debye temperature θ_d, which takes into account the difference in molar mass of the two compounds. Such a procedure may lead to an appreciable error, especially in cases where the molar mass difference is substantial or if the lattice specific heat cannot be well described in the frame of a simple Debye model. This last point is precisely relevant to the $C_{latt}(T)$ behavior of RNi$_2$. As shown in Ref. 13 a good description of the lattice specific heat of LuNi$_2$ can be obtained only under the assumption that θ_d depends on temperature in the range 220–280 K. Therefore, in order to achieve a correct evaluation of the lattice contribution to the specific heat, we prepared using the above-mentioned conditions the Gd$_{1-x}$Y$_x$Ni$_2$ ($x=0,0.2$) compounds and their nonmagnetic analogs Lu$_{1-y}$Y$_y$Ni$_2$ with the same molar masses. Measurements of the specific heat as well as ac magnetic susceptibility were performed using a Quantum Design PPMS-6000 system; the dc magnetization and susceptibility were measured by using a Quantum Design MPMS 5XL magnetometer.

Figure 1(a) shows the temperature dependencies of the specific heat of GdNi$_2$ and its nonmagnetic analog Lu$_{0.794}$Y$_{0.206}$Ni$_2$. For GdNi$_2$ a distinct anomaly is observed at $T_c \sim 75$ K while the specific heat for the reference compound increases continuously with increasing temperature. The sharp peak at $T_c \sim 75$ K on the $C_p(T)$ curve of GdNi$_2$ is associated with the magnetic ordering temperature. As follows from the inset in Fig. 1(a), at the same temperature a sharp fall of the ac susceptibility is observed. The Lu$_{0.794}$Y$_{0.206}$Ni$_2$ compound exhibits a paramagnetic behavior with a weak temperature dependence of the magnetic susceptibility, which is associated with Pauli paramagnetism. The Curie temperature observed for GdNi$_2$ is close to that ob-
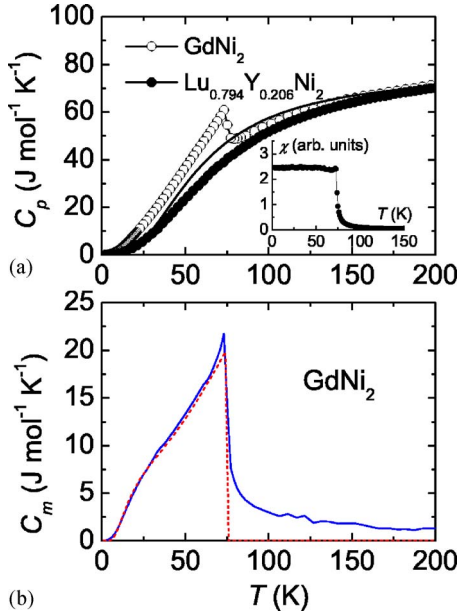
FIG. 1. (Color online) (a) Temperature dependence of the specific heat for GdNi$_2$ and its nonmagnetic partner Lu$_{0.794}$Y$_{0.206}$Ni$_2$. The solid line corresponds to the nonmagnetic specific heat calculated with γ=5.2 mJ mol^{-2} K^{-2} and θ_d=241 K. The inset shows the temperature dependence of the ac susceptibility for GdNi$_2$. (b) Magnetic part of the specific heat for GdNi$_2$ as a function of temperature (solid line). The dashed line shows the $C_m(T)$ dependence calculated in the molecular field approximation.

tained in previous works from specific heat measurements [73.7 K (Ref. [14]) and 75.3 K (Ref. [15])]. Bulk magnetization and susceptibility data for our GdNi$_2$ were found to be well consistent with those published by Yano *et al.*[6] The specific heat of Lu$_{0.794}$Y$_{0.206}$Ni$_2$ includes the lattice and electronic contributions only, $C_p(T)=C_{el}+C_{latt}=\gamma T+C_{latt}$. In view of the closeness of molar masses of GdNi$_2$ and Lu$_{0.794}$Y$_{0.206}$Ni$_2$ compounds, we assume that the sum $C_{el}+C_{latt}$ is the same for both compounds. Therefore, the magnetic contribution C_m to the specific heat of GdNi$_2$ may be obtained by a simple subtraction procedure. The temperature variation of this magnetic contribution is presented in Fig. 1(b) by a solid line. The dashed line corresponds to the $C_m(T)$ dependence calculated in the molecular field approximation assuming that only the Gd subsystem contributes to the magnetic specific heat. It turns out that the magnetic contribution to the specific heat of GdNi$_2$ persists well above the magnetic ordering temperature. The presence of spin fluctuations and short-range magnetic order above T_c was also revealed in previous electrical resistivity measurements[16] of GdNi$_2$.

In Fig. 2 we plot C/T versus T^2 in the low-temperature region for both GdNi$_2$ and Lu$_{0.794}$Y$_{0.206}$Ni$_2$ compounds. In this temperature interval $C_p(T)$ can be presented for both compounds as a sum of T-linear and T^3 terms. There is clear evidence that these compounds exhibit significantly different values of the T-linear specific heat coefficient γ. We find that γ=22 mJ mol^{-1} K^{-2} for GdNi$_2$ and γ=5.2 mJ mol^{-1} K^{-2} for the nonmagnetic analog, respectively. The γ value for Lu$_{0.794}$Y$_{0.206}$Ni$_2$ is close to that obtained experimentally for YNi$_2$ [5.2 (Ref. [17])] and LuNi$_2$ [5.4 (Ref. [18]) and 6.58 (Ref.

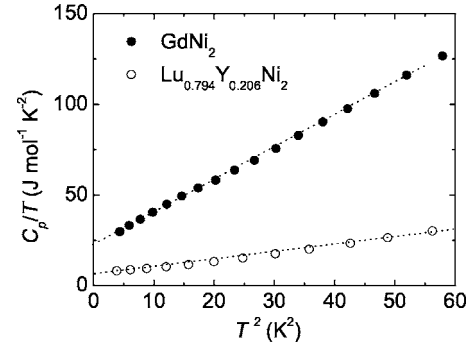FIG. 2. C_p/T versus T^2 dependencies of GdNi$_2$ and Lu$_{0.794}$Y$_{0.206}$Ni$_2$.

[13])] and to the value 3.67 estimated from density of states (DOS) calculations[19] for YNi$_2$ (all values are in mJ mol^{-1} K^{-2}). The Gd 4f electron states are located far below the Fermi level E_f, and do not contribute to the DOS at E_f. Therefore, the difference in the observed γ values may be associated with (i) the change in DOS near E_f due to the 3d band splitting originating from magnetic ordering of GdNi$_2$; (ii) the presence of an additional contribution from spin fluctuations induced by f-d exchange in the Ni 3d electron subsystem; and (iii) the electron magnon enhancement. The Fermi level in RNi$_2$ compounds was found to be located on the flat part of the DOS curve $N(E)$ with a relatively low DOS value.[20] This, together with the low value of the magnetic moment measured on Ni atoms implies only a weak change of $N(E_f)$ through the magnetic transition. As to the increase of γ caused by the electron-magnon mass enhancement, it was estimated to be about 10% for pure Gd.[21] This cannot explain such a large difference assuming that the electron-phonon enhancement of γ is the same for GdNi$_2$ and Lu$_{0.794}$Y$_{0.206}$Ni$_2$. Therefore, one can suggest that the additional contribution to the γ value in GdNi$_2$, $\Delta\gamma=\gamma_{GdNi_2}-\gamma_{(Lu,Y)Ni_2}$, results from spin fluctuations induced by f-d exchange in the 3d electron subsystem of Ni.

It is worth noticing that a strong influence of spin fluctuations induced by f-d exchange was observed for other Gd$_n$Ni$_m$ compounds.[22] In particular, the γ value for Gd$_3T$ with T=Ni,Co was found to be about one order of magnitude higher (γ=100–170 mJ mol^{-1} K^{-2}) than that obtained for isostructural Y$_3T$ compounds (γ=11–15 mJ mol^{-1} K^{-2}).[23,24] From the slope of the C/T versus T^2 dependence of Lu$_{0.794}$Y$_{0.206}$Ni$_2$ (Fig. 2) we estimated the Debye temperature to be equal to 241 K. The $C_p(T)=C_{el}+C_{latt}$ dependence calculated within the Debye model and using this θ_d value and γ=5.2 mJ mol^{-1} K^{-2} is shown by the solid line in Fig. 1. As can be seen, such a procedure is not applicable for the description of the nonmagnetic contribution to the total specific heat of GdNi$_2$. As to the increased slope of the C/T versus T^2 dependence for GdNi$_2$, it may result from the T^3 spin wave contribution because of an antiferromagnetic alignment of Gd and Ni magnetic moments.

Since the total entropy of GdNi$_2$ includes the electronic, lattice, and magnetic contributions

$$S = S_{el} + S_{latt} + S_m, \qquad (1)$$

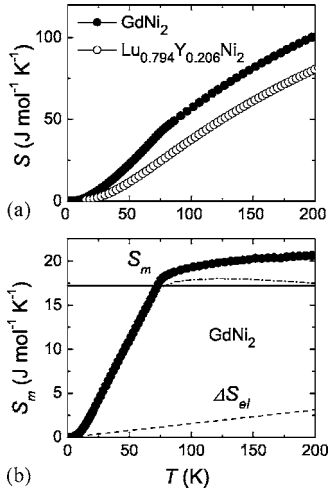the S_m value can be obtained by subtraction of the temperature dependencies of the entropy for GdNi$_2$ and

FIG. 3. (a) Temperature dependencies of entropies for $GdNi_2$ and $Lu_{0.794}Y_{0.206}Ni_2$. (b) Magnetic contribution to the entropy of $GdNi_2$. Dashed line indicates the additional electronic contribution to the entropy $\Delta S_{el} = \Delta \gamma T$; the chain line shows the temperature dependence of the magnetic entropy after subtraction of the additional contribution. Horizontal solid line corresponds to the maximal theoretical value $S_m^{theor} = R \ln(8)$ associated with Gd.

$Lu_{0.794}Y_{0.206}Ni_2$: $S = S_{GdNi_2} - S_{(Lu,Y)Ni_2}$. The $S(T)$ curves calculated by integration of $C_p(T)/T$ versus T dependencies for both compounds and the difference $S_m(T)$ are displayed in Figs. 3(a) and 3(b). Unlike previous specific heat studies,[14,15] we obtain that the magnetic entropy of $GdNi_2$ above the Curie temperature exceeds substantially the maximal theoretical value $S_m^{theor} = R \ln(2J+1) = 17.29$ J mol^{-1} K^{-1}, which was calculated assuming that only Gd ions have a magnetic moment. The S_m value obtained for $GdNi_2$ reaches ~ 20.6 J mol^{-1} K^{-1} with increasing temperature up to 200 K. Bearing in mind the presence of the above-mentioned discrepancy in the γ values, such an enhanced difference between the entropies for $GdNi_2$ and its nonmagnetic partner observed above T_c may be associated with an additional contribution to the first term in Eq. (1), i.e., $S_{el} = (\gamma_0 + \Delta \gamma)T$. Here we suppose that the γ_0 value for $GdNi_2$ is equal to $\gamma_{(Lu,Y)Ni_2}$ and it is determined by the DOS value at the Fermi level. Assuming that the value of $\Delta \gamma$ does not depend on the temperature we plotted this additional contribution to the entropy $\Delta S_{el} = \Delta \gamma T$ in Fig. 3(b) by a dashed line. As it turns out, the magnetic entropy obtained after subtraction of ΔS_{el} from the $S_m(T)$ becomes close to the expected value $S_m^{theor} = R \ln(8)$ above T_c [shown by solid line in Fig. 3(b)]. Therefore, one may conclude that in $GdNi_2$ the excess of the magnetic entropy above T_c originates from additional spin-fluctuation contributions induced by f-d exchange. It should be noted however, that $C_p(T)$ for both magnetic and nonmagnetic compounds become identical at temperatures larger than 150 K [see Fig. 1(a)] which implies for $GdNi_2$ a decrease of $\Delta \gamma$ with increasing temperature.

In order to confirm these results we have also measured the specific heat of $Gd_{0.8}Y_{0.2}Ni_2$ and its nonmagnetic analog $Lu_{0.635}Y_{0.365}Ni_2$, which have nearly the same molar masses. $C_p(T)$ for these compounds are presented in Fig. 4(a). As

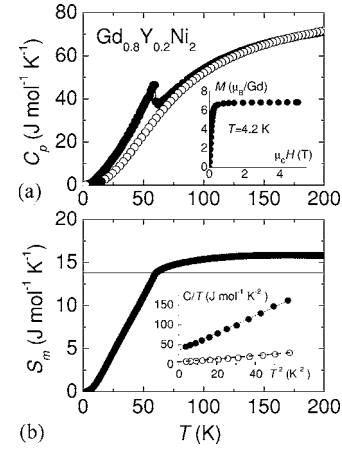FIG. 4. (a) Temperature dependence of the specific heat for $Gd_{0.8}Y_{0.2}Ni_2$ and its nonmagnetic partner $Lu_{0.635}Y_{0.365}Ni_2$. Inset shows the magnetization per Gd ion as a function of magnetic field at $T = 2$ K. (b) Magnetic contribution to the entropy of $Gd_{0.8}Y_{0.2}Ni_2$. Inset shows the C_p/T vs T^2 dependencies for $Gd_{0.8}Y_{0.2}Ni_2$ (full circles) and $Lu_{0.635}Y_{0.365}Ni_2$ (open circles). Horizontal line corresponds to the appropriate S_m^{theor} value for $Gd_{0.8}Y_{0.2}Ni_2$.

expected, the substitution of Y for Gd decreases the magnetic ordering temperature. For $Gd_{0.8}Y_{0.2}Ni_2$ the specific heat maximum which corresponds to the Curie temperature is observed at 60 K. The saturation magnetization of $Gd_{0.8}Y_{0.2}Ni_2$ calculated per Gd ion [see inset in Fig. 4(a)] is found to be $\sim 6.8 \mu_B$, which implies the presence of a small Ni magnetic moment in the opposite direction to that in the nondiluted $GdNi_2$. It should be noted that the total magnetization may also include the contribution from polarized conduction electrons and $5d$ electrons of Gd ions. Above 150 K, $C_p(T)$ becomes very close to that of $Lu_{0.635}Y_{0.365}Ni_2$. The magnetic part of the entropy calculated as in the previous case reaches a value of about 15.8 J mol^{-1} K^{-2} which surpasses substantially the expected value of 13.8 J mol^{-1} K^{-2} [see Fig. 4(b)]. The $Gd_{0.8}Y_{0.2}Ni_2$ compound exhibits also an enhanced value of the coefficient $\gamma = 34$ mJ mol^{-1} K^{-2} in comparison with the nonmagnetic reference 5.1 mJ mol^{-1} K^{-2} [shown in the inset in Fig. 4(b)]. These data support the results obtained for the nondiluted $GdNi_2$ compound.

In conclusion, the study of the specific heat of $Gd_{1-x}Y_xNi_2$ compounds with $x = 0$ and 0.2 and their nonmagnetic analogs $Lu_{1-y}Y_yNi_2$ with $y = 0.206$ and 0.365 has revealed that the difference between the entropies of magnetic and nonmagnetic compounds with the same molar masses surpasses substantially (by 14–19 %) the theoretical limit for the magnetic contribution $S_m = (1-x)R \ln(8)$ calculated under the assumption that only Gd ions have a magnetic moment. However, this additional magnetic contribution to the entropy seems to be underestimated since the retention of short-range magnetic order above the Curie temperature was not taken into account. Analysis of the specific heat behavior of some Gd compounds with nonmagnetic partners[25] has shown that at the magnetic ordering temperature, the magnetic entropy of Gd compounds reaches a substantially lower value (about 85%) than its expected limit. The same was observed for Gd metal.[26] At $T = 360$ K, i.e., well above the

Curie temperature ($T_c \sim 294$ K), the magnetic entropy of Gd metal reaches only 94% of its full value. These data allow us to suggest that in GdNi$_2$ the additional contribution to the magnetic entropy which originates in the Ni subsystem may reach 25–30 %. The values of the coefficient γ of the T-linear specific heat for Gd$_{1-x}$Y$_x$Ni$_2$ are observed to exceed significantly (by 4–6 times) the γ values for Lu$_{1-y}$Y$_y$Ni$_2$.

All these results suggest the presence of additional contributions arising from the Ni 3d electron subsystem and do not support a charge transfer model which implies the full filling of the 3d band in R-T intermetallics at high rare earth content. The enhanced magnetic entropy and γ value observed for Gd$_{1-x}$Y$_x$Ni$_2$ originate presumably from additional spin-fluctuation contributions induced by f-d exchange.

It should be emphasized that, in order to be convinced by the results obtained for GdNi$_2$ we have, in the present work, synthesized the Gd$_{0.8}$Y$_{0.2}$Ni$_2$ compound and its nonmagnetic analog with the same molar mass and performed specific heat measurements for these samples. We consider the enhanced magnetic entropy obtained for Gd$_{0.8}$Y$_{0.2}$Ni$_2$ as an additional confirmation of our data for GdNi$_2$. The results obtained in our work could not be explained by existing theories. We hope that our work will stimulate further theoretical investigations of the entropy content in rare earth–transition-metal compounds.

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