Disappearance of Magnetic Transition in (Ce,Gd)Ni$_5$ System

A. Dzubinska$^{a,b,*}$, J.R. Fernandez$^b$, M. Reiffers$^c$, J.I. Espeso$^b$, R. Varga$^d$ and J.C. Gómez Sal$^b$

$^a$Faculty of Science, Pavol Jozef Safarik University, Park Angelinum 9, 040 01 Kosice, Slovakia
$^b$Dept. of Earth Sciences and Condensed Matter Physics, University of Cantabria, Av. de los Castros s/n, 390 05 Santander, Spain
$^c$Faculty of Humanities and Natural Sciences, University of Presov, ul. 17 novembra 1, 081 16 Presov, Slovakia
$^d$CPM-TIP, UPJS, 041 54 Kosice, Slovakia

We present the results of an experimental study focused around CeNi$_5$ in the Ce$_x$Gd$_{1-x}$Ni$_5$ system. Pseudobinary bulk samples were prepared with concentration of $x = 0.85$, $0.9$, $0.95$, and $0.97$ by arc melting method. The structural analysis confirmed the CaCu$_5$ hexagonal crystal structure with P6/mmm space group and proved the existence of a single phase in all of them. The measurement of the magnetic properties shows that the increase of the Ce content leads to lower $T_C$ values. Above $x = 0.9$ spin fluctuations behaviour appears with a shoulder in $M(T)$ around $T = 130$ K. Heat capacity measurements support these observations.

DOI: 10.12693/APhysPolA.137.760

PACS/topics: physical properties, spin fluctuations, magnetic ordering

1. Introduction

The study of rare earth (RE) compounds has a long history because of their interesting physical properties due to 4f-localized magnetism, where competition between RKKY exchange interaction and Kondo effect is observed. One of these groups of compounds is RENi$_5$, for which some aspects have already been investigated [1–3]. In this series of rare earth materials Ni atoms are nonmagnetic, but they are very close to the onset of magnetism [4]. The whole class of these materials crystallizes in the CaCu$_5$-type hexagonal structure with P6/mmm space group [5]. Moreover, the compounds which consist of Ce are currently an interesting topic to explore because of quantum critical behavior and superconductivity observed in the proximity to a quantum critical point, a zero temperature transition between a magnetically ordered state and nonmagnetically ordered one [6].

In this work, in the course of systematic investigations of Ce-Gd-Ni$_5$ system, we report the evolution of the magnetic and thermodynamic properties of Ce$_x$Gd$_{1-x}$Ni$_5$ ($x = 0.85$, $0.9$, $0.95$, and $0.97$) polycrystalline compounds with applied magnetic fields. The main aim of this paper is to experimentally study the spin fluctuation (SF) effect on Ce/Gd substitution, and analyse the disappearance of the magnetic transition in the studied system, using for it different experimental methods.

2. Experimental details

Polycrystalline samples of Ce$_x$Gd$_{1-x}$Ni$_5$ ($x = 0.85$, $0.9$, $0.95$, and $0.97$) were synthesized by arc melting of the constituent elements having high purity (Ce — 99.9%, Gd — 99.9%, and Ni — 99.99%) in a stoichiometric ratio in a water-cooled Cu-hearth under purified argon atmosphere. In order to prepare single-phase materials with ensured homogeneity, each sample was turned and re-melted three times. The study of the crystal structure of all the prepared samples was carried out by X-ray diffraction (XRD) at a Brucker D8 Advance diffractometer. The XRD patterns were collected from 10° to 100°, 2θ-angle range with 0.02° steps, and an integration time of 0.5 s per step. The measurements of the magnetic properties $M(T,B)$ and the heat capacity $C_p(T,B)$ have been carried out in a PPMS® Quantum Design DynaCool® system (VSM and 2τ technique, respectively) under applied magnetic field up to 9 T. All the measurements were performed in the 2–300 K temperature range.

3. Results and discussion

New polycrystalline samples of Ce$_x$Gd$_{1-x}$Ni$_5$ with nominal compositions of $x = 0.85$, $0.9$, $0.95$, and $0.97$ were prepared and analyzed. Figure 1 shows the Rietveld refinement of the XRD pattern for Ce$_{0.97}$Gd$_{0.03}$Ni$_{5}$ as an example of the studied series. The results confirmed that all prepared samples crystallize in the CaCu$_5$ hexagonal crystal structure, so that the Vegard’s law can be applied. The lattice parameters slightly change their values. With the increase of the Ce content, the unit cell is expanding, which is consistent with the larger Ce volume with regard to Gd.
Disappearance of Magnetic Transition in (Ce, Gd)Ni₅ System

Fig. 1. Rietveld refinement of the powder X-ray diffractogram for Ce₀.97Gd₀.03Ni₅. The experimental data are presented with points and the calculation with a line. All the reflections, presented with vertical tick marks are indexed with the hexagonal CaCu₅ crystal structure. The difference pattern is presented at the bottom of the plot.

Fig. 2. Temperature dependence of the ZFC-FC magnetization of Ce₀.85Gd₀.15Ni₅ under three different applied magnetic fields. The inset shows the dM/dT derivative, fixing the T_C and the CW fit.

In order to study magnetic properties, the temperature dependence of ZFC-FC (zero field cooling-field cooling) magnetization at three different magnetic fields has been measured. The low temperature detail of ZFC-FC measurement of Ce₀.85Gd₀.15Ni₅ is displayed in Fig. 2. At the smallest magnetic field a ferromagnetic transition temperature has been observed at T_C = 4.9 K, and verified by the derivative dM/dT plot (shown in the inset of Fig. 2). An applied magnetic field of 1 T wipes out this transition. In the high temperature range, no trace of spin fluctuations is observed, and the magnetization follows the Curie-Weiss (CW) law. The effective paramagnetic moment μ_eff, and the paramagnetic Curie temperature θ_p were determined. For Ce₀.85Gd₀.15Ni₅ the effective paramagnetic magnetic moment is μ_eff = 4.56 μ_B/f.u., which is between the theoretical value for Ce³⁺ (2.54) and Gd³⁺ (7.94). The θ_p value is negative (−74.33 K), which indicates the presence of antiferromagnetic interaction in this sample. The same kind of analysis has been performed for all the studied concentrations, and the obtained values are presented in Table I.

The ZFC-FC magnetization of the Ce₀.95Gd₀.05Ni₅ sample is presented in Fig. 3. A minimum is visible at small applied magnetic field in mode in the low temperature range around T = 20 K (Fig. 3a). The upturn below 20 K can be explained as the superposition of the contribution coming from spin fluctuations and another from paramagnetic origin. This analysis is determined and displayed in the inset of Fig. 3a. At this point, it is interesting to note that earlier studies of pure CeNi₅ [7, 8] do not show minimum at low temperatures in the magnetic susceptibility. In the present

![Table I](image)

Experimental values determined for CeₓGd₁₋ₓNi₅ (x = 0.85, 0.9, 0.95 and 0.97). Transition temperature T_C, paramagnetic Curie temperature θ_p, effective paramagnetic moment μ_eff, and Sommerfeld coefficient γ₉{T at 9 T.

| x     | 0.85 | 0.9  | 0.95 | 0.97 |
|-------|------|------|------|------|
| T_C [K] | 4.9  | —    | —    | —    |
| θ_p [K] | −74.33 | −132.48 | −81.49 | −31.09 |
| μ_eff [μ_B/f.u.] | 4.56 | 3.03 | 3.01 | 2.49 |
| γ₉{T [mJ/(mol K²)]} | 42 | 42 | 42 | 43 |

Fig. 3. (a) Temperature dependence of the ZFC-FC magnetization at B = 0.01 T for Ce₀.95Gd₀.05Ni₅. The inset shows the calculated contributions. (b) Temperature dependence of the ZFC-FC magnetization for Ce₀.95Gd₀.05Ni₅ at two different magnetic fields. The inner inset shows the Curie-Weiss fit.
Fig. 4. Magnetic field dependence of the magnetization for Ce$_{x}$Gd$_{1-x}$Ni$_5$ at $T = 2$ K.

Fig. 5. Heat capacity measurements at different applied magnetic fields for Ce$_{0.85}$Gd$_{0.15}$Ni$_5$. The inset shows the low temperature detail, where the magnetic transition temperature at 4.9 K is better observed.

In pure CeNi$_5$, SF have been noticed at $T = 100$ K as a maximum in the magnetic susceptibility [9]. Here, the situation is similar, but the results indicate that Gd doping on CeNi$_5$ shifts the spin fluctuation contribution to higher temperatures. The inset of Fig. 3b presents the Curie-Weiss fit with the corresponding obtained parameters, which are in agreement with the expected results. Finally, no magnetic transition has been detected down to $T = 2$ K.

In Fig. 4 the magnetization as a function of applied magnetic field up to 9 T at $T = 2$ K is presented for all the studied compounds to see the influence of the Gd substitution. The value of the saturation magnetization is decreasing with the increasing Ce content. This is in agreement with previous studies of RENi$_5$ [3, 5].

4. Conclusions

Arc melting method was used for preparation Ce$_{x}$Gd$_{1-x}$Ni$_5$ ($x = 0.85, 0.9, 0.95,$ and 0.97). The samples crystallize in the hexagonal crystal structure CaCu$_5$ type. A magnetic transition was only observed for the sample with $x = 0.85$. Transition temperatures $T_C$, paramagnetic Curie temperatures $\theta_P$, effective paramagnetic moments $\mu_{\text{eff}}$, and Sommerfeld coefficients $\gamma$ as function of the Ce content were determined from magnetic and heat capacity measurements. Heat capacity below to 2 K would be convenient to use to determine the heat capacity measurements were performed from 2 K up to 300 K in applied magnetic fields up to 9 T. In Fig. 5 $C_p(T)$ is presented for Ce$_{0.85}$Gd$_{0.15}$Ni$_5$, as an example of the studied samples. The magnetic ordered state is observed at 4.9 K in agreement with the magnetic measurements. One can see, that the applied magnetic field depresses the intensity of the maximum, smears it out and shifts it to higher temperatures, as it is expected in ferromagnetic materials. High temperature values for the whole series follow the Dulong-Petit law ($C_p = 3R \sim 150$ J/(molK)). The Sommerfeld coefficients have been estimated from dependences $C_p/T$ vs. $T^2$ at an applied magnetic field of $B = 9$ T. These values are summarized in Table I.

The disappearance of the magnetic transition in (Ce,Gd)Ni$_5$ can be explained in Fig. 6. For the $x = 0.85$ sample, the low temperature contribution arises from the magnetically ordered state, previously detected in the magnetization measurements. On the other hand, the samples with $x = 0.95$ and 0.97 exhibit a clear non-magnetic behaviour, reminiscent of normal Fermi liquids. It is then noteworthy that only the sample with an intermediate composition ($x = 0.9$) follows a $-\ln(T)$ dependence. This behaviour may indicate that the studied system at this concentration is close to a quantum critical point, although to confirm this hypothesis further measurements are needed.
the Sommerfeld coefficients more precisely. The measurements of neutron diffraction could confirm the magnetic structure in the vicinity of magnetic ordering of the doped (Ce,Gd)Ni$_5$ system.

Acknowledgments

This work was supported by the projects VEGA 2/0032/16, VEGA 1/0956/17, VEGA 1/0611/18, VEGA 1/0053/19, APVV-16-0079 and the Spanish MINECO MAT2017-83631-C3-R. One of the authors A. Dzubinska would like to acknowledge the grant from Slovak Academic Information Agency (SAIA) under National Scholarship program.

References

[1] M. Reiffers, M. Della Mea, E. Bauer, G. Pristas, M. Vasilova, J. Phys. Soc. Jpn. 76, 68 (2007).
[2] A. Bajorek, G. Chelkowska, A. Chrobak, Intermetallics 32, 384 (2013).
[3] A. Dzubinska, M. Reiffers, J.I. Espeso, J.R. Fernandez, Acta Phys. Pol. A 131, 4 (2017).
[4] V.M.T.S. Barthem, D. Gignoux, A. Nait-Saada, D. Schmitt, G. Creuzet, Phys. Rev. B 37, 1733 (1988).
[5] F. Kayzel, Ph.D. thesis, Van der Waals-Zeeman Institute, Amsterdam 1997.
[6] R. Tripathi, D. Das, C. Geibel, S.K. Dhar, Z. Hossain, Phys. Rev. B 98, 165136 (2018).
[7] D. Ginoux, J.C. Gomez Sal, J. Appl. Phys. 57, 3125 (1985).
[8] M. Coldea, D. Andreica, M. Bitu, V. Crisan, J. Magn. Magn. Mater. 157, 627 (1996).
[9] M. Zapotokova, I. Curlik, M. Giovannini, M. Reiffers, Eur. Phys. J. B 86, 129 (2013).