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Disappearance of Magnetic Transition in (Ce,Gd)Ni_5 System

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We present the results of an experimental study focused around $CeNi_5$ in the $Ce_xGd_{1-x}Ni_5$ system. Pseudo-binary 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.

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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 behaviour 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 $Ce_xGd_{1-x}Ni_5$ ($x = 0.85$, 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.

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2. Experimental details

Polycrystalline samples of $Ce_xGd_{1-x}Ni_5$ ($x = 0.85$, 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 $Ce_xGd_{1-x}Ni_5$ 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.

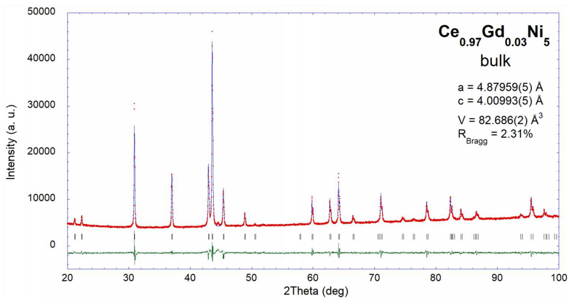

Fig. 1. Rietveld refinement of the powder X-ray diffractogram for $Ce_{0.97}Gd_{0.03}Ni_5$. The experimental data are presented with points and the calculation with a line. All the reflections, presented with vertical tick marks are indexed with the hexagonal $CaCu_5$ crystal structure. The difference pattern is presented at the bottom of the plot.

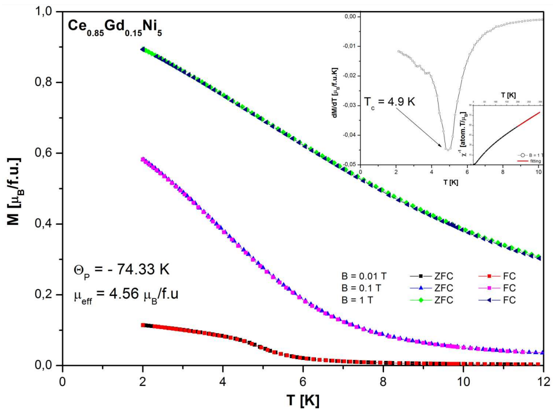

Fig. 2. Temperature dependence of the ZFC-FC magnetization of $Ce_{0.85}Gd_{0.15}Ni_5$ under three different applied magnetic fields. The inset shows the $\mathrm{d}M/\mathrm{d}T$ derivative, fixing the T_C and the CW fit.

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 $Ce_{0.85}Gd_{0.15}Ni_5$ 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 $\mathrm{d}M/\mathrm{d}T$ 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 $Ce_{0.85}Gd_{0.15}Ni_5$ the effective paramagnetic magnetic moment is $\mu_{\mathrm{eff}} = 4.56\ \mu_B$/f.u, which is between the theoretical value for Ce^{3+} (2.54) and Gd^{3+} (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.

TABLE I

Experimental values determined for $Ce_xGd_{1-x}Ni_5$ ($x = 0.85$, 0.9, 0.95 and 0.97). Transition temperature T_C, paramagnetic Curie temperature θ_P, effective paramagnetic moment μ_{eff}, and Sommerfeld coefficient γ_{9T} 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
γ_{9T} [mJ/(mol K^2)]	42	42	42	43

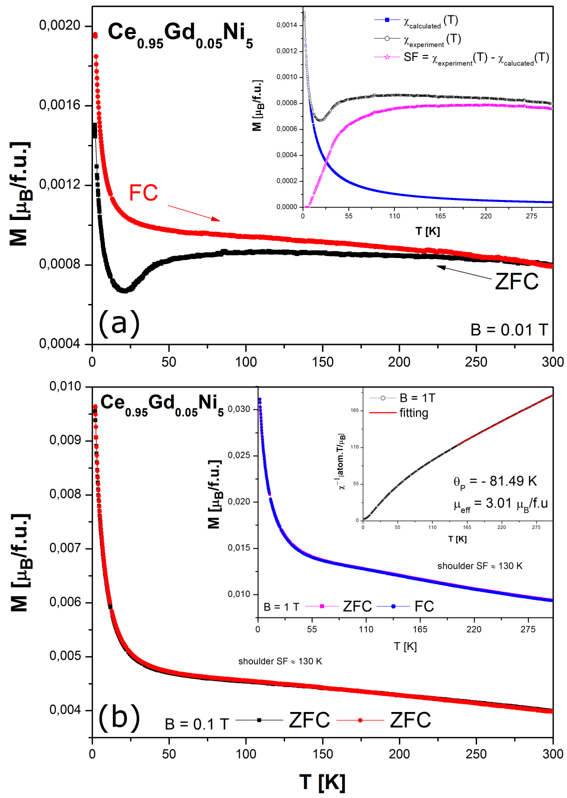

Fig. 3. (a) Temperature dependence of the ZFC-FC magnetization at $B = 0.01$ T for $Ce_{0.95}Gd_{0.05}Ni_5$. The inset shows the calculated contributions. (b) Temperature dependence of the ZFC-FC magnetization for $Ce_{0.95}Gd_{0.05}Ni_5$ at two different magnetic fields. The inner inset shows the Curie-Weiss fit.

The ZFC-FC magnetization of the $Ce_{0.95}Gd_{0.05}Ni_5$ 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 $CeNi_5$ [7, 8] do not show minimum at low temperatures in the magnetic susceptibility. In the present

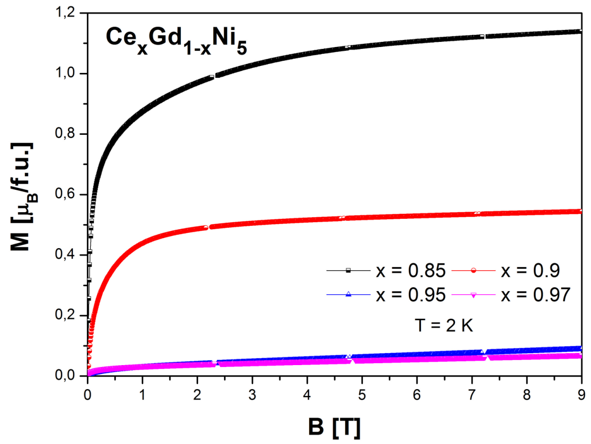

Fig. 4. Magnetic field dependence of the magnetization for $Ce_xGd_{1-x}Ni_5$ at $T = 2$ K.

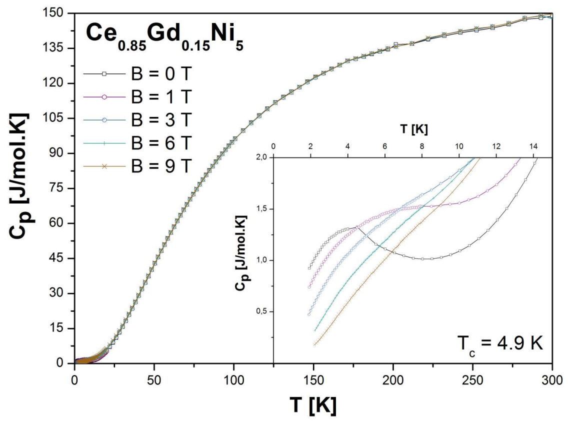

Fig. 5. Heat capacity measurements at different applied magnetic fields for $Ce_{0.85}Gd_{0.15}Ni_5$. The inset shows the low temperature detail, where the magnetic transition temperature at 4.9 K is better observed.

sample, by increasing the magnetic field, the minimum disappears, as it is observed for $B = 0.1$ T in Fig. 3b, and $B = 1$ T in the inset of Fig. 3b. Nevertheless, a small shoulder related with spin fluctuations could be observed at around $T = 130$ K at $B = 0.1$ T and 1 T. 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 dopping 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].

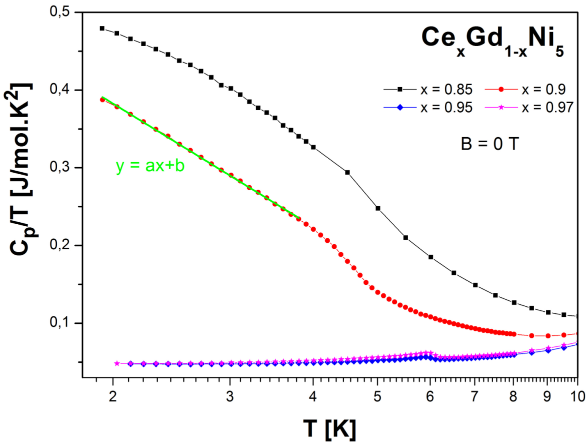

Fig. 6. C_p/T vs. $\log(T)$ plot for $Ce_xGd_{1-x}Ni_5$ at $B = 0$ T.

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.

4. Conclusions

Arc melting method was used for preparation $Ce_xGd_{1-x}Ni_5$ ($x = 0.85$, 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 θ_P, effective paramagnetic moments μ_{eff}, and Sommerfeld coefficients γ 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 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

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