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Magnetic and Heat Capacity Study of the new $Gd_{1-x}Ce_xNi_5$ Series

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We have prepared a new system of $Gd_{1-x}Ce_xNi_5$ polycrystalline samples with concentrations $x = 0$, 0.2, 0.5, and 0.8 in order to study the influence of different rare-earths substitutions on the ground state connected with spin fluctuations. $GdNi_5$ is a ferromagnetic compound with $T_C = 31.8$ K and $CeNi_5$ is a well-known spin fluctuation compound without magnetic ordering down to the lowest temperatures. X-ray diffraction study confirms the hexagonal crystal structure and the single phase samples. Magnetic properties ($M(T), M(B)$) show that an increasing content of Ce depresses the transition temperature, T_C, down to 4.9 K for $x = 0.8$. The heat capacity measurements confirmed these results.

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1. Introduction

The intermetallic compounds $RENi_5$ (RE = rare earths) crystallize in the simple $CaCu_5$-type hexagonal structure [1]. Their physical properties are rather well understood by considering their crystalline electric field (CEF) effect and exchange interactions. In this series, the Ni atoms are nonmagnetic, although they are very close to the onset of magnetism [2]. However, $CeNi_5$ is a Stoner enhanced paramagnet characterized by the influence of spin fluctuations (SF) on its properties [3], where SF originate from the Ni atoms [4]. On the other hand, $GdNi_5$ is known as a ferromagnetic compound with $T_C = 31.8$ K [5–7], where one can expect a doublet CEF ground state. Therefore, $Gd_{1-x}Ce_xNi_5$ is an interesting intermetallic system, where it is possible to study the competition of SF interactions and CEF effects.

In order to study the disappearance of the spin-fluctuation effect in $CeNi_5$ and the evolution of the magnetic CEF ground state, we have prepared and studied the physical properties of the polycrystalline samples of the new pseudobinary $Gd_{1-x}Ce_xNi_5$ series with $x = 0$, 0.2, 0.5, and 0.8.

2. Experimental details

The polycrystalline $Gd_{1-x}Ce_xNi_5$ samples were prepared by arc melting in an argon atmosphere with Ce concentration $x = 0$, 0.2, 0.5, and 0.8. The high purity elements Gd (99.6%), Ce (99.999%), Ni (99.999%) were taken in the proper stoichiometric ratio. In order to ensure homogeneity and to prepare single-phase materials, each alloy was turned upside down and re-melted three times.

The phase analysis of the prepared samples was performed by X-ray diffraction (XRD) (Bruker D8 Advance). The Fullprof software was used to analyze the X-ray diffraction patterns. The measurements of magnetic properties (*M(T), M(B)* and heat capacity $C(T, B)$ were carried out in a Quantum Design DYNACOOL device under applied magnetic fields up to 9 T. All measurements were performed in the temperature range 2–300 K.

3. Results and discussion

Figure 1 shows the powder XRD pattern of $Gd_{0.2}Ce_{0.8}Ni_5$ (as an example of the series) recorded at room temperature along with its structural Rietveld refinement. The results confirmed that all $Gd_{1-x}Ce_xNi_5$ studied samples crystallize in the hexagonal crystal structure of $CaCu_5$ type, so that the Vegard law can be applied. Determined lattice parameters are summarized in Table I. Data for $GdNi_5$ are in an agreement with previous data [2, 5–7]. We observed only a small decrease of a and a small increase of c with increase of Ce content. Therefore, we can expect that the main contribution to the change of the physical properties in this series is due to a change of the electronic properties.

We have measured the temperature dependences of ZFC–FC (zero field cooling–field cooling) magnetization at magnetic fields 0.01, 0.1, and 1 T for all samples. The measured magnetic properties of $GdNi_5$ are again in a very good agreement with previous data in literature [2, 5–7]. At a small applied magnetic field, $B = 0.01$ T, a maximum with a small hysteresis is present at $T_C = 31$ K. An applied magnetic field of 1 T smears out the maximum and produces an inflexion point at the same transition temperature. In the temperature range from above the transition up to room temperature, the magnetization follows the Curie–Weiss (C–W)

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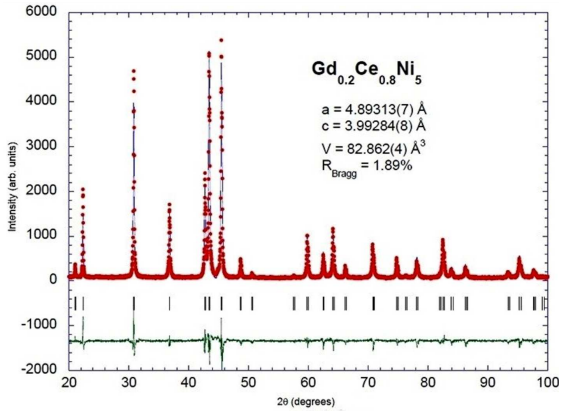

Fig. 1. Rietveld refinement of the XRD from the $Gd_{0.2}Ce_{0.8}Ni_5$ sample. The indexed reflections correspond to the $CaCu_5$ type hexagonal crystal structure.

law. We determined the effective magnetic moment as $\mu_{\text{eff}} = 7.95\ \mu_{\text{B}}$/f.u., which is the same as theoretical value for Gd^{3+} (7.94). The determined positive characteristic temperature is $\Theta_p = 26.8$ K, which is connected with ferromagnetic interaction.

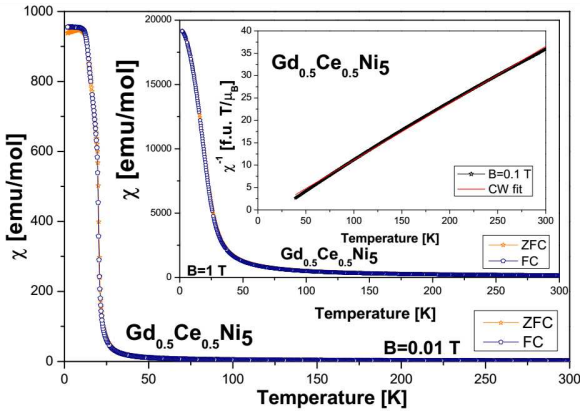

Fig. 2. Temperature dependence of the ZFC–FC magnetization of $Gd_{0.5}Ce_{0.5}Ni_5$ for different applied magnetic fields. There is a reciprocal of the susceptibility $\chi^{-1}(T)$ with C–W fit in the inset.

In order to show the characteristic behaviour of the magnetization for the rest of compositions, we present the dependence observed for $Gd_{0.5}Ce_{0.5}Ni_5$ in Fig. 2. In all samples, the high temperature dependence of $\chi(T)$ follows a Curie–Weiss law and the behaviour at low temperatures is also similar like in Fig. 2. The determined values of μ_{eff} and Θ_p are summarized in Table I. We observed that the effective magnetic moment μ_{eff} is decreasing with the increase of Ce content, as expected. However, we observed a change of Θ_p from positive to negative for 80% of Ce (antiferromagnetic interaction). We did not observe the appearance of characteristic maxima in magnetization at about 100 K, connected with spin fluctuations, which is observed in $CeNi_5$ [3, 4]. This points to the fact that 80% of Ce is not enough to depress the magnetic ordering. In order to find the concentration with completely depressed magnetic ordering it is necessary to prepare sample with $x > 0.8$. For small applied field 0.01 T and only for $x = 0.5$ we observed a second transition at ≈ 11 K apart from the magnetic transition at $T_{\text{C}} = 19.1$ K. This transition disappears for higher applied fields and it is not present also in heat capacity measurements. Therefore, we suppose that as well it could be due to spin rearrangement. However, further measurements are necessary in order to confirm it.

In Fig. 3, the magnetization as a function of the applied magnetic field at 2 K is presented for all compounds to see the Ce influence. The saturated magnetization for $GdNi_5$ is in agreement with previous data [6, 7]. The values of M_{SAT} are decreasing with increase of x, reaching 1.33 μ_{B}/f.u. for $x = 0.8$. We could explain it as a result of Gd/Ce substitution due to the lower Ce contribution to total magnetization.

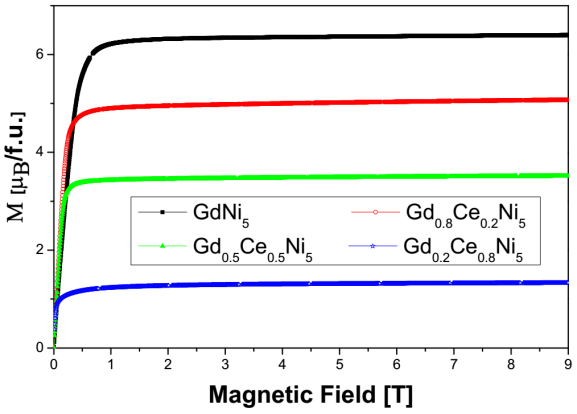

Fig. 3. Characteristic behaviour of the magnetic field dependence of the magnetization for $Gd_{1-x}Ce_xNi_5$.

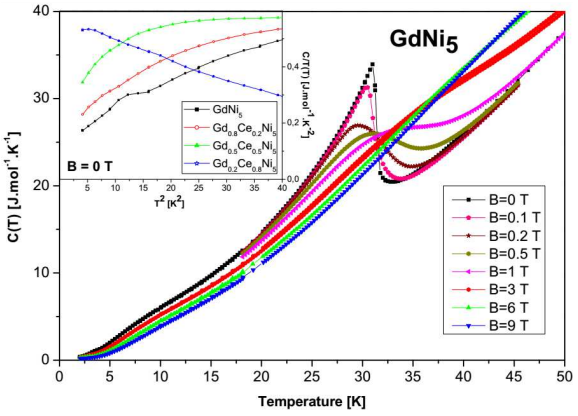

Fig. 4. Low temperature detail of the heat capacity of $GdNi_5$ as a function of the applied magnetic field. Inset: $C(T)/T$ vs. T^2 dependences for all samples in $B = 0$ T.

In Fig. 4, the low temperature detail of the heat capacity measurement on $GdNi_5$ under different applied magnetic fields is presented. We observe an anomaly at $T_{\text{C}} = 31$ K, which is the trademark of transition into the magnetically ordered state, in agreement with previous

data [2, 5–7]. One can see that the applied magnetic field is depressing the intensity of the peak without changing its position. The small observed shoulder at around 8 K could be attributed to the CEF effects — increase of population of the 8 levels of the ground state multiplet of Gd^{+3} ions with increase of temperature [6]. This anomaly was observed for $x = 0.2$ and 0.5, too, and does not disappear at higher applied magnetic fields.

We observe a similar behaviour for all the studied compositions. In order to manifest the influence of the Ce substitution, we present, in Fig. 5, the heat capacity at low temperatures as a function of the composition, showing the decrease of the transition temperature with the increasing Ce content under no applied magnetic field. Moreover, one can see that the intensity of the maximum is simultaneously smeared out. The observed transition temperatures are shown in Table I. The high temperature behaviour for all the concentrations shows saturation at room temperature, which is close to value of 150 J/(mol K), as it is expected from the Dulong–Petit law.

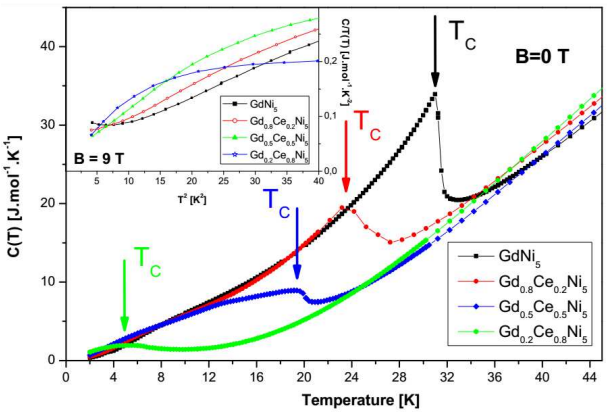

Fig. 5. Low temperature detail of the heat capacity for different compositions at $B = 0$ T. Inset: $C(T)/T$ vs. T^2 dependences for all samples at $B = 9$ T.

TABLE I

Summary of the experimental values determined for $Gd_{1-x}Ce_xNi_5$ ($x = 0$, 0.2, 0.5, 0.8): transition temperature T_C, the Sommerfeld coefficient γ, paramagnetic Curie temperature Θ_p and effective moment $\mu_{\rm eff}$ and lattice parameters.

x	0	0.2	0.5	0.8
T_C [K]	31	23.5	19.5	4.9
$\gamma_{9\ T}$ [mJ/(mol K^2)]	22.2	29.9	29.3	23.9
Θ_p [K]	26.8	21.2	12.5	-21.4
$\mu_{\rm eff}$ [μ_B/f.u.]	7.95	6.96	5.93	4.17
a [nm]	0.491	0.491	0.49	0.489
c [nm]	0.397	0.397	0.398	0.399
V [nm^3]	0.083	0.083	0.083	0.083

In order to determine the electronic Sommerfeld coefficient γ, we performed the extrapolation analysis of the $C(T)/T$ vs. T^2 dependences. We observed that, in zero applied magnetic field, the magnetic contribution to the heat capacity is present in all the compositions at 2 K (inset of Fig. 4) γ changes from 122 up to 530 mJ mol^{-1} K^{-2} with increase of Ce content. However, there is no heavy-fermion behaviour. We suppose it is due to presence of magnetic contribution. The analysis at an applied magnetic field of 9 T (the magnetic contribution is already depressed — inset of Fig. 5) yielded values that varied between 22 and 29 mJ/(mol K^2), in agreement with previously reported data [2, 5–7].

4. Conclusions

We have prepared new polycrystalline pseudobinary compounds of the $Gd_{1-x}Ce_xNi_5$ ($x = 0$, 0.2, 0.5, 0.8) system by arc melting. The samples crystallize in the hexagonal $CaCu_5$-type structure. We observed that the magnetic transition temperature decreases from 31 K to 4.9 K with the increasing Ce content. From susceptibility measurements there are estimated the effective moments, which decrease when Ce content increases. The temperature dependences of the heat capacity show transition temperatures in agreement with the magnetic measurements. In order to determine more precisely the Sommerfeld coefficients without magnetic contribution it is necessary to measure the heat capacity below 2 K.

Acknowledgments

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