Vol. **113** (2008) *ACTA PHYSICA POLONICA A* No. 1

Proceedings of the CSMAG'07 Conference, Košice, July 9–12, 2007

# Specific Heat of the $Tb_{1-x}La_xNi_2$ Solid Solutions

J. Ćwik, T. Palewski

International Laboratory of High Magnetic Fields and Low Temperatures
Gajowicka 95, 53-421 Wrocław, Poland

and K. Nenkov*

Institut fur Festkörper- und Werkstofforschung Dresden
Postfach 270016, 01171 Dresden, Germany

Specific heat measurements have been performed on the polycrystalline $TbNi_2$, $LaNi_2$ and their solid solutions $Tb_{1-x}La_xNi_2$ ($x = 0.2$, 0.3). The Debye temperatures, phonon and conduction electron contributions as well as the magnetic part of the heat capacity were determined and discussed. The magnetocaloric effect was estimated from measurements performed in a magnetic field of 0.42 T for $TbNi_2$, $Tb_{0.8}La_{0.2}Ni_2$ and $Tb_{0.7}La_{0.3}Ni_2$.

PACS numbers: 75.30.Sg, 75.40.–s, 74.70.Ad

## 1. Introduction

Specific heat measurements constitute a very useful tool for investigating the magnetic properties of rare-earth solid solutions. In the solid solutions $Tb_{1-x}La_xNi_2$, the substitution of Tb ions having non-zero magnetic moment for non-magnetic lanthanum ions leads to the suppressing long-range magnetic order of Tb ions. $TbNi_2$ is a typical Curie–Weiss paramagnet and at the relatively low temperature it is ferromagnetically ordered. According to the latest information the Curie temperature of $TbNi_2$ is 36 K [1]. $LaNi_2$ exhibits only the Pauli paramagnetism in a temperature range of 4–300 K [2]. It should be noted that $TbNi_2$ and its solid solutions with such properties as the low temperatures of magnetic ordering and high saturation magnetization show promise as materials for new magnetic-refrigerator designing.

## 2. Experimental

$Tb_{1-x}La_xNi_2$ solid solutions were prepared as described in [2]. The samples were characterized by using powder X-ray diffractograms. The heat capacity mea-

*On leave from W. Trzebiatowski Institute of Low Temperature and Structure Research, Polish Academy of Sciences, P.O. Box 1410, 50-950 Wrocław, Poland.

surements were performed in the temperature range of 2–295 K in zero and 0.42 T applied magnetic fields using Quantum Design PPMS 14 Heat Capacity System.

## 3. Result and discussion

X-ray diffraction patterns of powder $Tb_{1-x}La_xNi_2$ samples were characterized by reflections corresponding to the cubic $C15$ superstructure (space group $F\bar{4}3m$). The lattice parameters of $TbNi_2$, $Tb_{0.8}La_{0.2}Ni_2$, $Tb_{0.7}La_{0.3}Ni_2$, and $LaNi_2$ were determined to be equal to 1.432, 1.441, 1.445, and 1.472 nm, respectively.

The heat capacity for metallic system can be considered as the sum of independent electron $C_{\rm el}(T)$, phonon $C_{\rm ph}(T)$, and magnetic contributions $C_{\rm mag}(T)$. Based at the results suggested by Palewski et al. [3] and the method proposed by Bouvier et al. [4] we have taken as the lattice contributions data of $LuNi_2$ after multiplying the temperature values. The Debye temperatures and the $\gamma$ parameter for $TbNi_2$, $Tb_{0.8}La_{0.2}Ni_2$, and $Tb_{0.7}La_{0.3}Ni_2$ were calculated using the Debye function in the temperature range 100–200 K and there were obtained the values $\Theta_{\rm D}$ = 261 K, 260 K, and 259 K, respectively. The best fitting for this temperature range could be obtained if the parameters $\gamma$ = 17.5 mJ/(mol K$^2$). $C_{\rm tot}(T)$, the sum of electron and phonon $C_{\rm el+ph}(T)$ and magnetic contributions of $TbNi_2$ compounds are shown in Fig. 1. Figure 1a exhibits the dependences measured in zero magnetic field; Fig. 1b shows the dependences measured in applied magnetic fields of 0.42 T, respectively. The sharp $\lambda$-kind maxima at $T$ = 36 K on the heat capacity curves correspond to the temperatures of the magnetic ordering of the $TbNi_2$ (Fig. 1). The similar $\lambda$-kind maxima for $Tb_{0.8}La_{0.2}Ni_2$ and $Tb_{0.7}La_{0.3}Ni_2$ are observed at 32 K and 28 K, respectively. The heat capacity of $TbNi_2$ measured in magnetic field of 0.42 T (see Fig. 1b) show that the applied field causes the broadening and displacement of the maximum and decrease in its amplitude. For both measured $Tb_{1-x}La_xNi_2$ solid solutions the similar behavior was observed.

The magnetic part of the entropy $S_{\rm mag}$ was calculated according to [2] and the results are given in Fig. 2. The analysis shows that the magnetic entropy does not reach the theoretical maximum value $S_{\rm mag}^{\rm max} = R\ln(13)$ at low temperature region. This fact and the fact that a marked magnetic contribution to heat capacity persists up to at least 100 K suggest very probably the existence of the spin fluctuations far above the magnetic ordering temperature. It should be noted that the entropy of solid solutions studied tends to saturation at $T > 250$ K and approaches the theoretical maximum value. Such behavior of the magnetic entropy can be explained by features in the ground-state level splitting by crystal field (CF). The cubic CF splits the $^7F_6$ ground state multiplet of the $Tb^{3+}$ in $TbNi_2$ compounds into six sublevels; among them, $\Gamma_1$ (singlet) ground state, $\Gamma_4$ (triplet) and $\Gamma_5^2$ (triplet) are separated from others $\Gamma_2$ (singlet), $\Gamma_5^1$ (triplet) and $\Gamma_3$ (doublet) by a substantial energy gap [5] and only low lying sublevels give contribution to the values of magnetic entropy. The magnetocaloric effect was

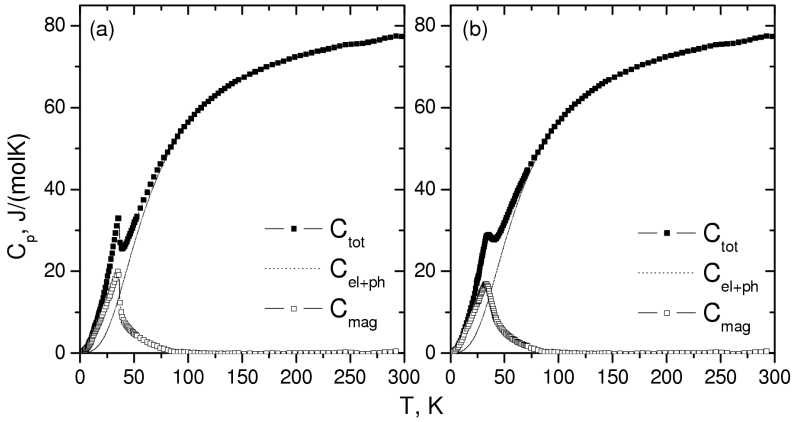


Fig. 1. The heat capacity of $TbNi_2$ measured in zero magnetic field (a) and 0.42 T magnetic field (b).

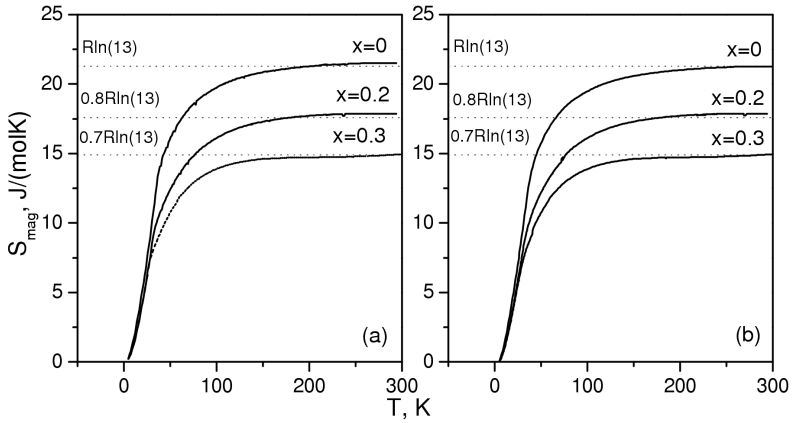


Fig. 2. Magnetic part of the entropy $S_{\mathrm{mag}}$ of $Tb_{1-x}La_xNi_2$ ($x = 0$, 0.2, 0.3) measured in zero magnetic fields (a) and 0.42 T magnetic field (b). The dotted lines indicate the $(1-x)R\ln(13)$ limits.

calculated as described in Ref. [6]. In the case of the 0.42 T magnetic field, the magnetocaloric effect for $TbNi_2$ and its solid solutions is very low. The maximum magnetocaloric effect $-\Delta T_{\mathrm{ad}}$ for $TbNi_2$ reaches 0.7 K near 36 K, for $Tb_{0.8}La_{0.2}Ni_2$ reaches 0.55 K near 32 K, and 0.65 K for $Tb_{0.7}La_{0.3}Ni_2$ near 28 K. At the $-\Delta T_{\mathrm{ad}}$ curve, in the case of $TbNi_2$, we have observed the existence of any anomaly within the magnetically ordered state at about 14 K. The anomaly is probably associated with a spin reorientation on some of the Tb sites in the superstructure. Similar anomaly was described by Gratz et al. [1]. It is likely that the use of high magnetic fields can result in an increase in the magnetocaloric effect.

## 4. Conclusion

The heat capacity measurement confirm that the substitution of La for Tb decreases the magnetic ordering and the results are comparable with data of the magnetic studies. The magnetocaloric effect estimated in 0.42 T magnetic field did not give such big values, which allow the technical application of these solid solutions.

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