

# Magnetic entropy changes and relative cooling powers in $Gd_xLa_{1-x}Ni_5$ compounds

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Magnetic properties and magnetocaloric effects were studied in  $Gd_xLa_{1-x}Ni_5$  compounds. The Curie temperatures decrease from  $T_C = 35$  K in  $GdNi_5$  to 9K for a sample with  $x = 0.2$ . The maximum entropy changes, in field of  $H = 7$  T, vary from 12.8 J/kgK ( $x=1.0$ ) to 5.5 J/kgK ( $x = 0.2$ ). In high external field, linear dependences of the maxima in the entropy changes on  $H^{2/3}$  were shown as expected for compounds which show a second order type magnetic transition. The relative cooling power in field of 7 T, decreased from 347 J/kg ( $x = 1.0$ ) to 80 J/kg ( $x = 0.2$ ).

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## 1. Introduction

The magnetic refrigeration, based on magnetocaloric effect (MCE), is an efficient and environment-friendly procedure, as compared with gas-compression refrigeration technology [1-3]. The magnetocaloric effect is an intrinsic property of magnetic materials, induced via the coupling of a magnetic system with an applied magnetic field. Since of their possible technical uses, the magnetic materials, expected to have large magnetocaloric effects, were intensively studied. The adiabatic temperature change

$dT = -\frac{T}{c_{H,p}} \left( \frac{\partial M}{\partial T} \right)_{H,p}$  is proportional to the partial

derivative of the magnetization,  $M$ , versus temperature  $T$ ,  $c_{H,p}$  being the heat capacity at constant magnetic field,  $H$  and pressure,  $p$ . The magnetocaloric effect is measured in terms of isothermal magnetic entropy change,  $\Delta S$ , and/or adiabatic temperature change,  $\Delta T$ [1-4].

The magnetocaloric effect was analysed mainly in connection with the magnetic phase transition, at the Curie temperature,  $T_C$ . Relative large entropy changes were also found in ferrimagnetic compounds, where high variation of magnetizations in some temperature range, particularly around the compensation points can be seen [5]. The  $dM/dT$  values are higher when the magnetization shows first order magnetic transition. These materials have also hysteretic properties that can deteriorate MCE under the cycle of the magnetization-demagnetization process. Thus, the researches have been focused also on materials which show second order type transition. In these systems, by using the molecular field model, has been shown that the maxima in entropy changes,  $-\Delta S_{max}$ , follow on the external field, a  $H^{2/3}$  dependence [6, 7].

The main working materials used in magnetic refrigeration prototypes are based on gadolinium alloys [3]. Gadolinium is an S-state ion having a magnetic moment,  $M_{Gd}=7 \mu_B$ , when neglecting the Gd5d band polarization.

The Curie temperature of the Gd metal,  $T_C \cong 293$  K, can be significantly changed by alloying with various elements. In this way the location of maximum in entropy change can be tuned.

In this paper we report the magnetocaloric properties of  $Gd_xLa_{1-x}Ni_5$  compounds. The effects of gadolinium substitution by lanthanum on the entropy changes are analysed.

## 2. Magnetic and magnetocaloric properties

The  $Gd_xLa_{1-x}Ni_5$  compounds were prepared by levitation method and then the samples were thermally treated at  $T=1000$  °C. The compounds crystallize in a hexagonal structure of  $CaCu_5$ -type. The magnetic measurements were performed in the temperature range 2-300 K and fields up to  $H = 9$  T [8].

The  $Gd_xLa_{1-x}Ni_5$  compounds with  $x \geq 0.2$  are ferrimagnetically ordered. In the above system,  $LaNi_5$  ( $x=0$ ) shows a spin fluctuations behaviour [9]. As the lanthanum is substituted by gadolinium a small magnetic moment is induced at nickel sites through 4f-5d-3d exchange interactions [10,11]. The nickel moments are antiparalelly oriented to those of gadolinium ones and decrease from  $\cong 0.2 \mu_B$  ( $x = 1$ ), being nearly nil at  $x = 0.2$ . Small nickel moments were also reported in other rare-earth-nickel intermetallic compounds [12, 13].

The magnetization isotherms for  $Gd_xLa_{1-x}Ni_5$  compounds with  $x = 0.6$  and  $0.2$  are given in Fig. 1. The magnetizations, at 2 K are saturated in fields higher than 6 T.

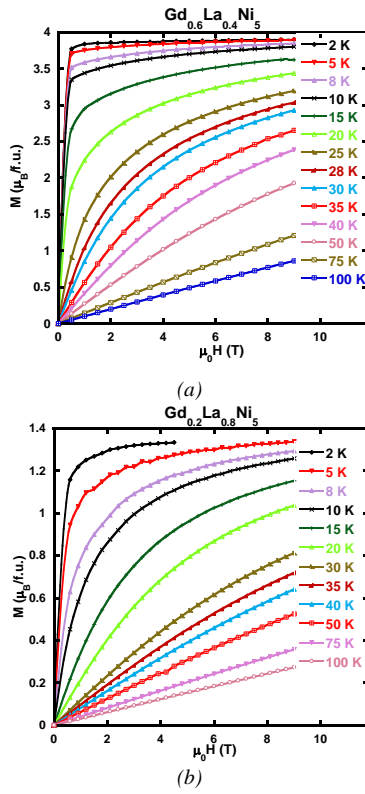


Fig. 1. Magnetization isotherms for  $Gd_xLa_{1-x}Ni_5$  compounds with  $x = 0.6$  (a) and  $x = 0.2$  (b).

The Curie temperatures decrease nearly linearly from  $T_C = 35$  K ( $x = 1$ ) as gadolinium is gradually substituted by lanthanum – Fig. 2.

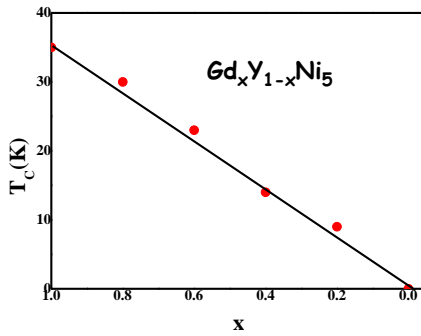


Fig. 2. Composition dependence of the Curie temperatures.

The entropy changes have been determined from magnetization isotherms by using the Maxwell relation. Because of the slow scan rate of the magnetic field, the conditions in obtaining the data can be considered as isothermal, rather than adiabatic. The entropy change associated with the change of magnetization, is given as:

$$\Delta S(T, H) = \int_0^H \left( \frac{\partial M}{\partial T} \right)_H dH \quad (1)$$

From magnetization isotherms, obtained at constant temperature and successive values of the applied field  $H$ ,

with step  $\Delta H_i$ , the Maxwell equation can be approximated by the relation:

$$\Delta S = \sum_i \frac{M_{i+1} - M_i}{T_{i+1} - T_i} \Delta H_i \quad (2)$$

We denoted by  $M_{i+1}$  and  $M_i$  the magnetizations measured in field  $H$ , at temperatures  $T_{i+1}$  and  $T_i$ , respectively.

The entropy changes,  $\Delta S$ , in  $Gd_xLa_{1-x}Ni_5$  were computed from magnetization isotherms, according to the relation (2). The  $(-\Delta S)$  values, determined in the field ranges 0.6–9 T, for compositions  $x = 0.8, 0.6$  and  $0.2$  are plotted in Fig. 3. Similar dependences can be also seen for compositions having  $x = 1.0$  [14] and  $0.4$ . The maxima of entropy changes,  $-\Delta S_{\max}$ , in field of 7 T, decreased from 12.8 J/kgK in  $GdNi_5$  up to 5.5 J/kgK at composition with  $x = 0.2$ .

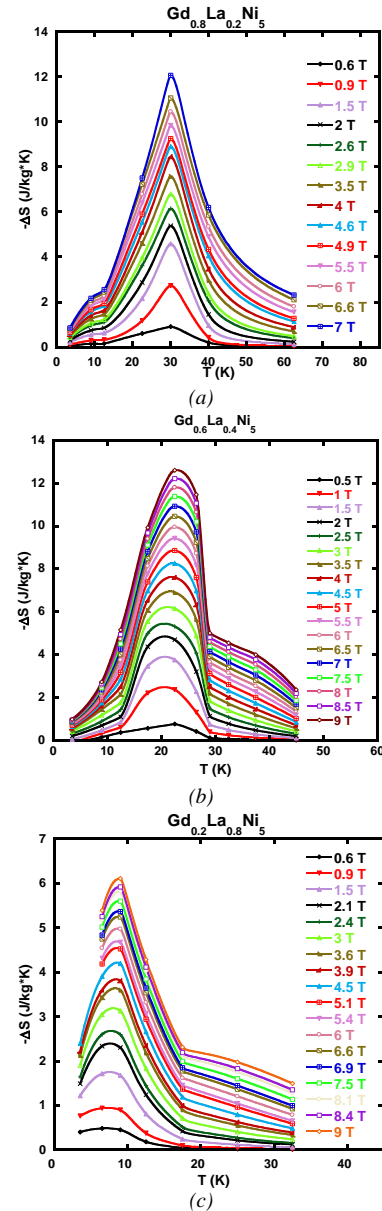


Fig. 3. Entropy changes as function of temperature and magnetic field, for  $Gd_xLa_{1-x}Ni_5$  compounds with  $x = 0.8, 0.6$  and  $0.2$ .

The  $-\Delta S_{\max}$  values increased with increasing external field according to a  $H^n$  law. In high field,  $H > 1.2$  T, the exponent is  $n = 2/3$ , in agreement with the predicted value by the mean field theory [6] – Fig. 4. In weak external field ( $H < 1.5$  T), the effective exponent  $n$  seems to be field dependent, as already observed [15]. In this region the power law is not valid.

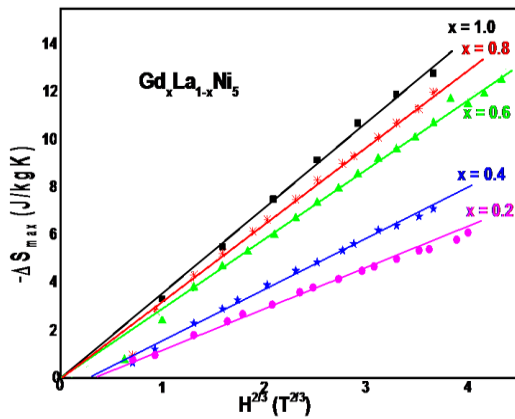


Fig. 4. The  $-\Delta S_{\max}$  values as function of  $H^{2/3}$ .

The  $(-\Delta S_{\max})$  vs  $H^{2/3}$  dependences pass through the origin of the reference frame for samples with  $x \geq 0.6$ . There is a negative intercept of  $(-\Delta S_{\max})$  for compounds with  $x = 0.2$  and  $0.4$ . According to Kuzmin et al [16], the maximum magnetic entropy change contains, beside the usual term in  $H^{2/3}$ , a small negative contribution, independent on  $H$ . Spatial inhomogeneity of the sample was considered to be the origin of this off-set term. Their magnitude was shown to be proportional to the width of the distribution of local Curie points.

Analysing the data from Figs. 2 and 3, for sample with  $x = 0.2$ , there seems really to be some sort of distribution of local Curie temperatures confirming the above prediction. Although the samples were carefully prepared, some small deviations from random distribution of gadolinium and lanthanum atoms on 1a type lattice sites of  $\text{CaCu}_5$  structure can be present.

The relative cooling power  $\text{RCP}(\Delta S)$  is an important quality factor of a refrigerant material, which is a measure of the amount of the heat transfer between the cold and hot reservoirs, in an ideal refrigerant cycle. The  $\text{RCP}(\Delta S)$  is defined as the product of the maximum value of the entropy change  $|\Delta S_{\max}|$  and the full-width at half-maximum,  $\delta T_m$  [1-3]. A large  $\text{RCP}(\Delta S)$  corresponds to a better magnetocaloric material. The  $\text{RCP}(\Delta S)$  value in  $\text{GdNi}_5$ , at 7 T, was 347 J/kg and decrease up to 270 J/kg in the sample with  $x = 0.8$ . For samples with higher lanthanum content, the corresponding  $\text{RCP}(\Delta S)$  are significantly smaller. The above values for compounds with  $x \geq 0.8$  are close to those previously reported in  $\text{Gd}_2\text{Ge}_2\text{Si}_2$  with  $\text{RCP}(\Delta S) = 305$  J/kg [17], but smaller than those determined in gadolinium (556 J/kg) [18] or in  $\text{Gd}_{68}\text{Ni}_{32}$  amorphous alloy with  $\text{RCP}(\Delta S) = 583$  J/kg [19].

There was also suggested that it is more convenient, for characterizing the magnetocaloric material, to use the

specific renormalized cooling power,  $\text{RCP}(\Delta S)/\Delta H$ , relative to external field variation  $\Delta H$ . The  $\text{RCP}(\Delta S)/\Delta H$  values are plotted in Fig. 5, for  $\Delta H$  ranges of 2, 4 and 7T, respectively as function of composition. Similar trend can be seen in all cases, although the  $\text{RCP}(\Delta S)/\Delta H$  values are somewhat higher for smaller external field,  $\Delta H$ , variations.

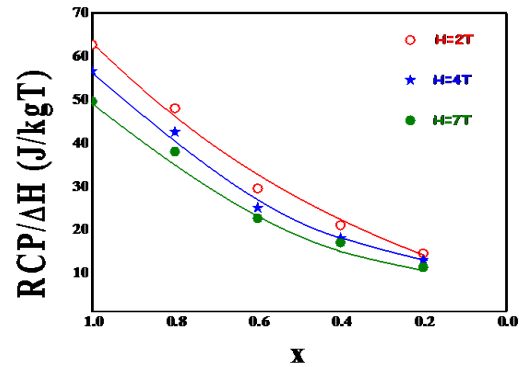


Fig. 5. The  $\text{RCP}(\Delta S)/\Delta H$  values as function of composition in the field ranges  $H \leq 2T$ ,  $H \leq 4T$  and  $H \leq 7T$ .

### 3. Conclusions

The maxima values of the entropy changes,  $|\Delta S_{\max}|$ , are located at the Curie points and decrease as the gadolinium content in a given sample is diminished. In the high field range these values follow a  $H^{2/3}$ -type dependence, as predicted for a second order type transition, by the mean field model. Relative small deviations from a random distribution of Gd and La atoms in 1a site of  $\text{CaCu}_5$ -type structure, can explain the small  $|\Delta S_{\max}|$  negative value at  $H=0$ . The relative cooling powers decrease nearly proportional with gadolinium content in a given sample.

### References

- [1] V. K. Pecharsky, K. A. Gschneidner, J. Appl. Phys. **86**, 566 (1999).
- [2] K. A. Gschneider, V. K. Pecharsky, A. O. Tsokol, Rep. Progr. Phys. **68**, 1479 (2005).
- [3] A. M. Tishin, J. Magn. Magn. Mater. **316**, 351 (2007).
- [4] E. Burzo, I. G. Pop, D. N. Kozlenko, J. Optoelectron. Adv. Mater. **12**, 1105 (2010).
- [5] E. Burzo, I. Balasz, I. Deac, R. Tetea, J. Magn. Magn. Mater. **322**, 1109 (2010).
- [6] H. Oesterreicher, F. T. Parker, J. Appl. Phys. **55**, 4334 (1984).
- [7] Q. Y. Dong, H. W. Zhang, J. L. Shen, J. R. Sun, B. G. Shen, J. Magn. Magn. Mater. **319**, 56 (2007).
- [8] E. Burzo, L. Chioncel, I. Costina, S. G. Chiuzbaian, J. Phys.: Condens. Matter **18**, 4861 (2006); E. Burzo, I. Costina, L. Chioncel, Mater. Sci. Forum **373-376**, 669 (2001).
- [9] E. Burzo, S. Chiuzbaian, I. Chioncel, A. Neumann, J. Phys.: Condens. Matter **12**, 5897 (2000); J. Phys. Condens. Mater **14**, 8057 (2002).
- [10] I. A. Campbell, J. Phys. F.: Metal Phys. **2**, L 147

- (1972).
- [11] E. Burzo, L. Chioncel, R. Tetean, O. Isnard, *J. Phys.: Condens. Matter* **23**, 026001 (2011).
- [12] E. Burzo, S. Chiuzbaian, M. Neumann, L. Chioncel, M. Valeanu, I. Creanga, *J. Appl. Phys.* **92**, 7362 (2002); E. Burzo, S. Chiuzbaian, L. Chioncel, A. Takacs, M. Neumann, I. Creanga, *Mold. J. Phys.* **5**, 50 (2006).
- [13] E. Burzo, C. Pacurar, I. Balasz, *Molec. Cryst. Liquid Cryst.* **415**, 523 (2004); E. Burzo, A. T. Pedziwiatr, W. E. Wallace, *Solid State Commun.* **61**, 57 (1987).
- [14] N. Bucur, E. Burzo, R. Tetean, *J. Optoelectron. Adv. Mater.* **10**, 801 (2008).
- [15] V. Franco, A. Conde, V. K. Pecharsky, K. A. Gschneidner *Europhys. Lett.* **79**, 47009 (2007).
- [16] M. D. Kuzmin, M. Richter, A. M. Tishin, *J. Magn. Magn. Mater.* **321**, 11 (2009).
- [17] V. Provenzano, A. J., Schapiro, R. D. Shull, *Nature* **429**, 853 (2004).
- [18] J. Shen, J. F. Wu, J. R. Sun, *J. Appl. Phys.* **106**, 003902 (2009).
- [19] X. C. Zhong, P. F. Tang, Z. W. Liu, D. C. Zeng, Z. G. Zeng, H. Y., Yu, W. Q. Qiu, M. Zou, *J. Alloys Comp.* **509**, 6889 (2011).

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