PHYSICAL REVIEW B **79**, 014428 (2009)

Percolation processes and spin-reorientation of $PrNi_{5-x}Co_x$

D. L. Rocco[*]
*Departamento de Física, Universidade Federal de Ouro Preto, 35400-000 Ouro Preto, MG, Brazil
and Departamento de Física and CICECO, Universidade de Aveiro, 3810-193 Aveiro, Portugal*

J. S. Amaral, J. V. Leitão, V. S. Amaral, and M. S. Reis
Departamento de Física and CICECO, Universidade de Aveiro, 3810-193 Aveiro, Portugal

R. P. Fernandes
*Institut für Keramische Hochleistungswerkstoffe, Technische Universität Hamburg-Harburg,
Denickestraße 15, D-21073 Hamburg, Germany*

A. M. Pereira and J. P. Araújo
Departamento de Física, IFIMUP, Universidade do Porto, 4150 Porto, Portugal

Nuno V. Martins and P. B. Tavares
Departamento de Química and CQ-VR, Universidade de Trás-os-Montes e Alto Douro, 5001-911 Vila Real, Portugal

A. A. Coelho
*Instituto de Física Gleb Wataghin, Universidade Estadual de Campinas-UNICAMP, Caixa Postal 6165,
13083-970 Campinas, São Paulo, Brazil*

(Received 26 March 2008; revised manuscript received 8 October 2008; published 22 January 2009)

In the present work we report on the structural and magnetic behaviors of the $PrNi_{5-x}Co_x$ intermetallic compounds. Due to the competition between the anisotropy energies of both Co and Pr sublattices, this series has a spin-reorientation phenomenon at low temperature (140 K). The Curie temperature, as a function of Co content, has a sudden increase above a critical concentration $x_c \sim 1.9$ and this feature is assigned as a percolation of geometrically spaced Co clusters. This assumption is explained based on the critical exponent of percolation theory. The series presents therefore a rich magnetic phase diagram, which could be established over a full doping range, i.e., from $x=0$ to $x=5$. We have also studied these compounds on the magnetocaloric point of view and found a quite large full width at half maximum (δT_{FWHM}) of the magnetic entropy change curves for some of the compositions, due to the merging of the ΔS peaks associated with the spin-reorientation process and the Curie temperature T_C. In addition, the series has an appreciable relative cooling power, which is therefore suitable to be used in a magnetic refrigerator operating in a large range of temperature.

DOI: 10.1103/PhysRevB.79.014428 PACS number(s): 75.30.Sg, 64.60.ah, 75.30.Gw

I. INTRODUCTION

The pseudobinary $PrNi_{5-x}Co_x$ compounds are derived from the parents $PrCo_5$ and $PrNi_5$ compounds. The Co-rich side is especially interesting due to its (i) high energy product (BH_{max}) compared with $SmCo_5$ (Ref. 1) and (ii) Curie temperature T_C higher than Nd-Fe-B magnets.[2] On the other hand, $PrNi_5$ compound is paramagnetic due to the high crystal field of this compound.[3] For intermediate concentrations, some authors[4–7] found for $RNi_{5-x}Co_x$ compounds (R: rare earth), with increase in Co content (i) a monotonic increase in the Curie temperature and the saturation value of the magnetization M_S, (ii) an abrupt change in T_C and M_S as a function of Co content near $x=2.0$, and (iii) a discontinuity in lattice parameters also around $x=2.0$. Some of these compounds $RNi_{5-x}Co_x$ also present a strong magnetocrystalline anisotropy and, consequently, some families show a spin-reorientation process.[8] Thus, we prepared samples of the $PrNi_{5-x}Co_x$ series with small compositional increment ($\delta x = 0.05$), belonging to the special compositional region between $x=2$ and $x=3$ in order to perform a detailed analysis of its magnetic and structural properties. We have chosen the praseodymium because $PrNi_5$ is the unique compound, among those RNi_5, which is paramagnetic,[9] and therefore this series $PrNi_{5-x}Co_x$ is the richest one from the magnetic point of view. For instance, its Curie temperature covers a wide temperature span. Finally, at the end of the paper, a brief analysis on the magnetocaloric potential of this series is presented.

II. SAMPLE PREPARATION AND STRUCTURAL CHARACTERIZATION

$PrNi_{5-x}Co_x$ ($x=1.95$, 2.07, 2.15, 2.20, 2.25, 2.30, 2.40, 2.45, 2.50, 2.55, and 3.00) samples were prepared by arc melting under a purified argon atmosphere, starting from the appropriate amounts of the constituent elements, namely, praseodymium (99.9%), nickel (99.995%), and cobalt (99.995%). Ingots were remelted up to three times to ensure homogeneity and then annealed in an evacuated quartz tube at 1020 K for 7 days, with a subsequent quench in liquid nitrogen. The weight loss was smaller than 0.5%.

In order to check homogeneity and stoichiometry of the samples, energy dispersive x-ray spectroscopy (EDS) tech-

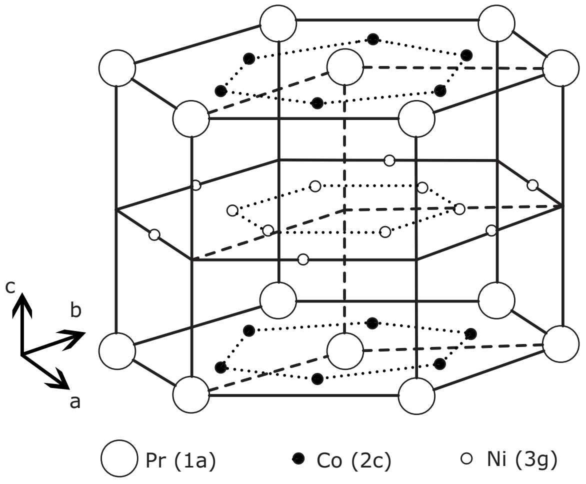

FIG. 1. Representation of the $CaCu_5$-type structure (taken from Ref. 10) for the $PrNi_3Co_2$ compound. The Co atoms preferentially occupy 2*c* sites rather than the 3*g* sites (Ref. 11).

nique was used and we could verify that the samples, after annealed, are single phase and, in addition, show a composition of the elements within 6% of the nominal value.

Phase purity and crystal structure of the samples were studied by x-ray powder diffraction using a multichannel detector x-ray diffractometer from Phillips with a Cu $K\alpha$ radiation. From Rietveld analysis we could conclude that the annealed samples crystallize in the hexagonal $CaCu_5$ ($P6/mmm$) type structure and the lattice parameters (at 300 K) are in good agreement with values found by Chuang *et al.*[5] and Andreyev *et al.*[6] for polycrystals and single crystals, respectively. Figure 1 shows a typical crystal structure; this crystal has two Co/Ni sites (3*g* and 2*c* Wyckoff symbols) and only one Pr site (1*a*) and this distribution for each site (3:2:1) is quite important for our analysis (Sec. III B).

Measurement of magnetization as function of magnetic field and temperature was carried out in two vibrating sample magnetometers (VSM): one for low temperature (up to 300 K; commercial machine: Cryogenic) and another for measurements at high temperature (300 K up to 900 K; homemade machine). Some measurements were also done in a superconducting quantum interference device (SQUID) magnetometer (commercial machine: Quantum Design).

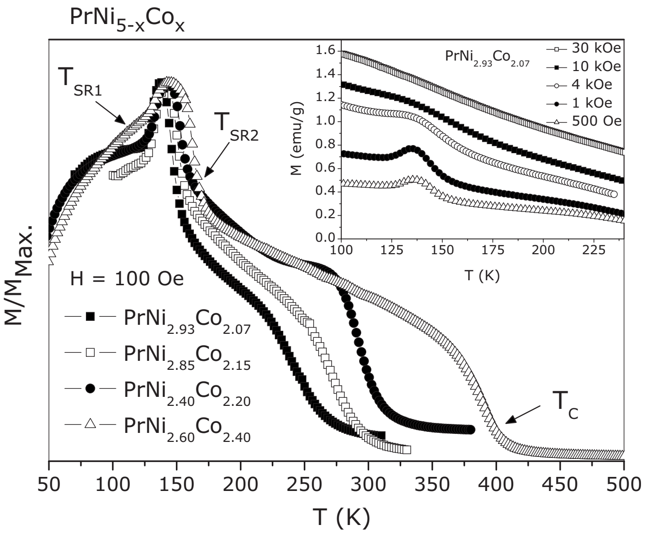

FIG. 2. Normalized magnetization as a function of temperature for four compounds of the series. The inset presents the magnetization as a function of temperature for several values of applied magnetic filed on the $PrNi_{2.93}Co_{2.07}$ compound. Above $H=30$ kOe the curves do not show remarkable spin-reorientation.

III. RESULTS AND DISCUSSIONS

A. Magnetic phase diagram

The anisotropy of the rare-earth ions is imposed by the shape of magnetic 4*f* electronic shell in such a way that ions with a positive second-order Steven's coefficient $\alpha_J > 0$ (Er and Sm) present an axial anisotropy (along *c* axis) and, consequently, reinforce the Co sublattice anisotropy (that is also along the *c* axis). On the other hand, rare-earth ions with $\alpha_J < 0$ (Pr, Nd, Tb, Dy, and Ho) tend to have an easy magnetization direction in the basal plane of the hexagonal structure. In the last case we have a coexistence of these two competing anisotropies, i.e., axial for the Co sublattice and planar (*a*-*b* plane) for the rare-earth sublattice.[12] This competition induces a spin-reorientation phenomenon in these compounds and rules some of the magnetic properties of these materials.

For temperatures below T_{SR1} the anisotropy of Pr sublattice is larger than that of Co sublattice and therefore the total magnetic moment lies in the basal plane (*a*-*b*).[6] Note that, in this case, the Pr and Co magnetic moments are collinear.[12] On the other hand, for temperature above T_{SR2} the anisotropy of the Co sublattice is higher and, consequently, the basal plane becomes the hard plane and the *c* axis becomes the easy magnetization direction.[6] Again, in this case, both magnetic moments are collinear.[12] For temperature ranging from T_{SR1} up to T_{SR2} there is a strong competition between the magnetocrystalline anisotropy of both sublattices (Pr and Co) and, consequently, the total magnetic moment assumes a cone arrangement between the basal plane and the *c* axis. In a different fashion as before the magnetic moment of those sublattices are noncollinear[12] for temperatures $T_{SR1} < T < T_{SR2}$. Thus, the spin-reorientation process occurs in a range of temperature ($T_{SR1} < T < T_{SR2}$) (Ref. 12) rather than in a specific temperature.

Measurements of magnetization as a function of temperature elucidate the above discussion; increasing temperature, T_{SR1} and T_{SR2} correspond to the first and second inflection points of the curves, as shown in Fig. 2 for the samples with $x=2.07$, 2.15, 2.20, and 2.40 (measurements for the other samples are similar to these). A strong dependence of the Curie temperature on Co content is also seen, and it changes from 250 K for $x=2.07$ to 390 K for $x=2.40$.

From the magnetization curves (and some data from literature[6]), we could build the magnetic phase diagram for this $PrNi_{5-x}Co_x$ series, as presented in Fig. 3. For low temperature the total magnetic moment lies in the *a*-*b* plane with increasing Co content up to $x \sim 3.5$ (estimated value from Ref. 6; half-filled up-triangle symbol). Above this concentration the total magnetic moment changes to the cone configu-

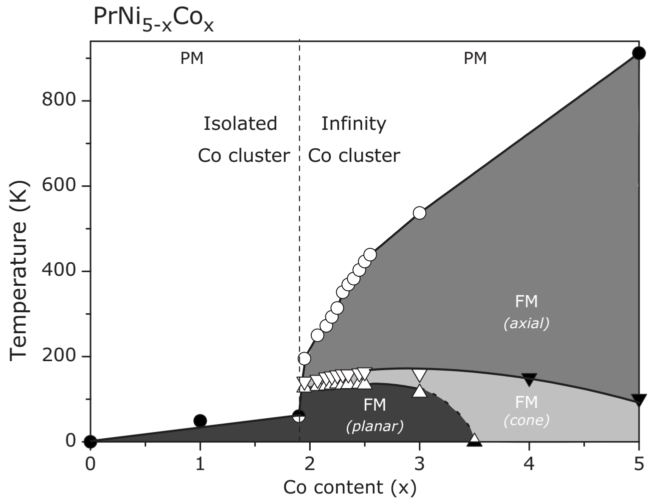

FIG. 3. Magnetic phase diagram of the PrNi$_{5-x}$Co$_x$ system. Open symbols: present work, closed symbols: Andreyev *et al.* (Ref. 6), and half-filled symbols: estimated. ○ and ●: Curie temperature, △ and ▲: T_{SR1} (the total magnetic moment changes from the basal plane to the cone arrangement), and ▽ *and* ▼: T_{SR2} (the total magnetic moment changes from the cone arrangement to c axis). Finally, FM stands for ferromagnetic and PM for paramagnetic.

ration. It is easy to understand because the magnetocrystalline anisotropy of Co sublattice increases due to increasing Co content and therefore its anisotropic energy is comparable to that of the Pr sublattice. On the other hand, increasing temperature for concentrations below $x_c \sim 1.90$ the system changes from the ferromagnetic order to a paramagnetic one. Note that substitution of Co into PrNi$_5$ (paramagnetic) leads to a linear (and slow) increase in the Curie temperature, changing from zero (for $x=0$) up to 60 K (for $x_c \sim 1.90$). This is reasonable because the critical temperature in these compounds is mainly ruled by Co-Co interaction and therefore Co substitution in the Ni site increases the overall Co-Co exchange interaction which leads to an increase in T_C. Above this critical concentration up to $x \sim 3.5$ (estimated value), considering a temperature increase, we can find first T_{SR1}, where the total magnetic moment changes from the *a*-*b* plane to the cone arrangement, and then T_{SR2}, where the total magnetic moment changes from the cone configuration to axial arrangement (c axis). Above T_{SR2} it is possible to find the Curie temperature. Above $x \sim 3.5$ the system at zero temperature has the total magnetic moment in the cone position and then changes at T_{SR2} to an axial configuration. Again, further increasing the temperature leads to a Curie temperature.

Note that just above x_c there is a sudden increase in T_C from 60 K at x_c to 912 K at PrCo$_5$. This feature is discussed below considering percolation theory.

B. Percolation processes

As discussed before, above x_c there is a sudden increase in the Curie temperature. Our hypothesis for this behavior is a percolative process. Below $x_c \sim 1.9$ there are spatially distributed isolated Co magnetic clusters with a short-range interaction. These clusters increase in size up to $x \sim 1.9$, which explains the linear $T_C(x)$ behavior. At $x \sim 1.9$ the percolation process between Co clusters takes place and therefore the interaction between Co ions changes and assumes a long-range order character, which is increasing faster the Curie temperature when x increases.

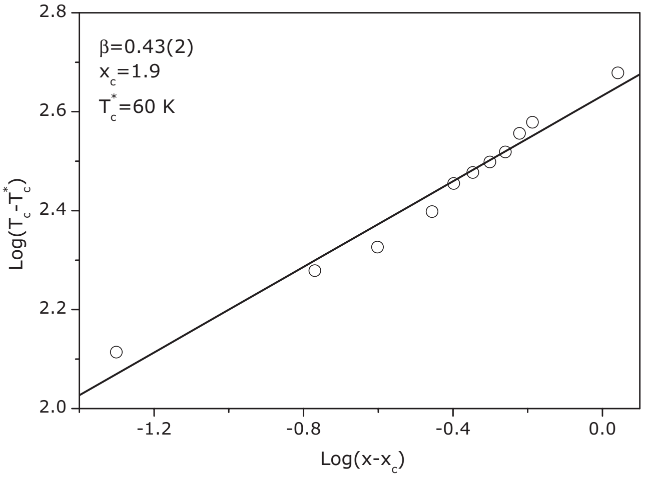

FIG. 4. Scaling of the Curie temperature data (from Fig. 3) to fit the equation $(T_C - T_C^*) \propto (x - x_c)^\beta$. We found $\beta = 0.43(2)$, while $\beta = 0.41$ is a signature of percolation process. Above, $T_C^* = T_C(x_c)$.

From the percolation theory[13] the probability P_∞ of a certain Co ion to be belong to the infinity cluster (that percolated) is given by $P_\infty \propto (x - x_c)^\beta$, where the parameter β is the critical exponent and must be 0.41 for a three-dimensional (3D) lattice (it is important to emphasize that this parameter does not depend on the geometry, while the critical concentration x_c does).[13] Since the Curie temperature is a measurement of the Co-Co exchange interaction and this interaction is ruled by the Co environment, we can write the following equation: $(T_C - T_C^*) \propto (x - x_c)^\beta$, where T_C^* is the Curie temperature at x_c, i.e., $T_C^* = T_C(x_c)$. This kind of equation was already written by other authors.[14] Thus, the critical exponent can be obtained from the slope of the log-log curve, as presented in the Fig. 4. We could obtain $\beta = 0.43(2)$ confirming therefore our hypothesis of percolation process of Co clusters.[14,13]

Another two facts ratify our percolation hypotheses as follows: (1) As widely known, the number of the Wyckoff symbols represents the number of ions that belong to a certain equivalent site for one formula unit, as can be seen in Fig. 1. In our case, considering PrNi$_5$, two Ni ions go into 2*c* site while three of them go into 3*g* site. However, Coroian *et al.*[11] and Zlotea and Isnard,[15] via neutron-scattering measurements, concluded that Co substitution preferentially occupies the 2*c* sites rather than the 3*g* sites. Thus, substituting Ni by Co, the Co ions go into 2*c* site up to the maximum allowed occupation of this site, i.e., two ions (that corresponds to $x = 2$). Thus, we can see Co layers [along the (001) plane] up to $x = 2$, and those are separated each other by Ni layers [along the (002) plane]. With further increasing the Co content, Co ions do not go into 2*c* site since it is already fully occupied; rather they go to the 3*g* site, connecting therefore the previously isolated Co layers. It is quite interesting to note that this critical concentration to connect Co clusters is exactly what we found ($x \sim 1.9$), above which the Co clusters

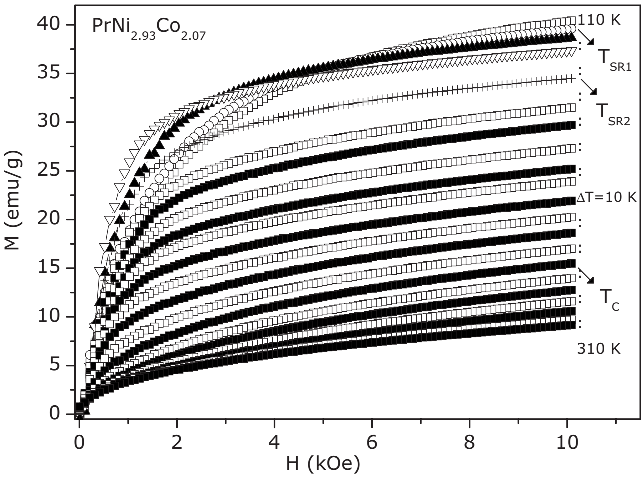

FIG. 5. Magnetization as a function of applied magnetic field around spin-reorientation temperatures T_{SR1} and T_{SR2} and Curie temperature T_C. For the sake of clearness, some isothermal curves are not shown.

are percolated. (2) The critical concentration x_c depends on the dimension and geometry of the lattice. Thus, the $R\mathrm{Ni}_{5-x}\mathrm{Co}_x$ series should have the same behavior with (almost) the same x_c since the lattice is the same (CaCu_5 type), and indeed it occurs. The compounds with Y, La, Sm, and Gd have the same behavior with $x_c \sim 2.0$,[4,16] and in the case of $\mathrm{SmNi}_{5-x}\mathrm{Co}_x$, those authors observed a remarkable coercivity around this concentration and addressed this effect to a possible clusterization.[17,18] Minor difference with other $R\mathrm{Ni}_{5-x}\mathrm{Co}_x$ systems can be assigned how the Co/Ni substitution occurs through those 3*g* and 2*c* sites. It is also important to note that the critical concentration does not match the value of a 3D hexagonal lattice ($x=3$) (Ref. 13) since the occupation runs in a two-dimensional (2D) regime. Thus, based on the considerations discussed above, we have divided the phase diagram in two parts: below x_c, with isolated Co clusters (these clusters are spatially distributed), and above x_c, with an infinite clusters in the system.

Another point that deserves attention is the existence of possible Griffiths phase[19] in this series. Summarizing Griffiths idea, let us consider, for instance, a 3D regular lattice with ferromagnetic arrangements between the spins localized in the vertices of the lattice. This system has a Curie temperature (generally called Griffiths temperature T_G). Upon either site or bond dilution it is intuitive of a decreasing of the Curie temperature since the magnetic interactions become weaker. Further dilution allows reaching the percolation concentration (values depend on the geometry of the lattice), below which there are only insulated clusters. The Griffiths phase lies in a temperature range above $T_C(p)$, i.e., the Curie temperature for a certain value of dilution p and below $T_G=T_C(p=1)$. Note the similarity of Griffiths ideas with the description of the phase diagram of the $\mathrm{PrNi}_{5-x}\mathrm{Co}_x$ series. We therefore propose a Griffiths phase for these compounds and a careful verification will be addressed in due time. This behavior was already observed in other materials,[20] including intermetallics.[21]

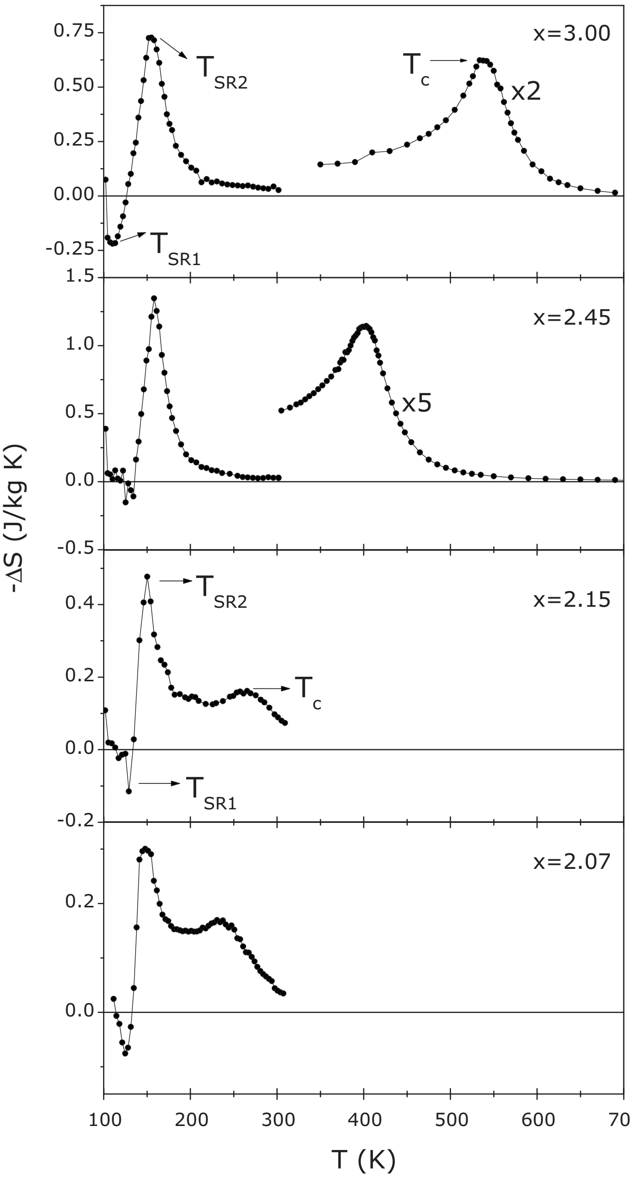

FIG. 6. Magnetic entropy change obtained from the magnetization as a function of magnetic field (see Fig. 5) for some of the samples prepared. Those peaks are associated to the spin-reorientation process (around T_{SR1} and T_{SR2}) and T_C. Note the high value of δT_{FWHM} around T_C (for higher Co concentration). Decreasing Co content the peaks around T_{SR2} and T_C merge, increasing δT_{FWHM}. For the sake of comparison, the magnetic entropy change curves around T_C were multiplied by a factor shown in each panel.

C. Advantage of the spin-reorientation to the magnetocaloric effect

From the magnetization curves as a function of the applied magnetic field at various temperatures and using the appropriate numerical approximation,[22] it is possible to determine the magnetic entropy change (ΔS) due to an external applied field change. Figure 5 presents typical isothermal magnetization curves for the sample $\mathrm{PrNi}_{2.93}\mathrm{Co}_{2.07}$. Note that the low-temperature isothermals (from 110 K up to 130 K) show a crossover at low values of magnetic field due to spin-reorientation. For higher values of temperature we found a monotonic decrease in the magnetization values, as expected. These features are reflected in the ΔS curves, as shown in the corresponding Fig. 6. We can see a negative peak (at T_{SR1}) that is related to plane to cone spin-reorientation, a second positive peak at T_{SR2} related to cone to axis spin-reorientation, and finally a positive peak associated to the para-ferro transition.

It is worth noting that the maximum at T_{SR2} is larger than that at T_C. This is ascribed to the fact that the magnetization around the spin-reorientation from cone to axis has a sharper change than that around the paramagnetic-ferromagnetic transition, as shown in Fig. 2. In addition, spin-reorientation processes are accompanied by a magnetostriction effect along the *c* axis,[6,15] increasing therefore the magnetocaloric potential.

The same procedure was applied to all of the samples prepared and the magnetic entropy change showed similar behavior. For the sake of clearness, Fig. 6 presents typical results of some of the samples. Let us focus our attention to the $x=3.0$ sample (top panel of Fig. 6). Similar to the one, the maximum magnetic entropy change around T_C is smaller than that around T_{SR2}. However, it is worthy to note the full width at half maximum δT_{FWHM} around $T_C=537$ K, reaches 88 K (for 10 kOe), whereas around $T_{SR2}=202$ K we found $\delta T_{FWHM}=34$ K. From the phase diagram it is expected that the peak related to T_{SR1} and T_{SR2} does not change in temperature, while it is expected a strong temperature dependence of the peak associated to T_C. Decreasing Co content, we found that the sample with T_C around room temperature is with the concentration $x \simeq 2.2$. Further decrease in Co content induces a merging of the magnetic entropy change peaks, i.e., that around T_C and around T_{SR2}. The onset concentration for the merged peaks occurs between $2.07 < x < 2.15$ and drastically increases the full width at half maximum δT_{FWHM} of both peaks.

Concerning the maximum magnetic entropy change ΔS_{max} around T_C, it remains approximately constant with Co doping. On the other hand, ΔS_{max} around the spin-reorientation has a strong dependence on Co substitution with a maximum at $x \sim 2.5$. The relative cooling power (RCP), defined as ΔS_{max} times δT_{FWHM}, is quite large for our compounds in spite of this low value of magnetic-field change (10 kOe). Calculated RCP for the sample with both peaks merged ($x=2.07$ for instance), reaches 30 J kg^{-1}, whereas this quantity for metallic Gd is 60 J kg^{-1} at the same conditions.[23] This is worthy to note that the RCP of Gd is only two times larger than $PrN_{5-x}Co_x$ while the maximum ΔS_{max} is 12 times bigger.

IV. SUMMARY

In the present work we prepared a set of samples with a small compositional increments ($\delta x \sim 0.05$) within the special concentration range $2 \lesssim x \lesssim 3$ of the $PrNi_{5-x}Co_x$ series. It is well established[12] that the competition between the anisotropy energy of Pr sublattice (that tends to align the magnetic moment in the basal *a*-*b* plane) and Co sublattice (that, on the contrary, tends to align the magnetic moment along the *c* axis) leads to spin-reorientation processes. In this sense, this series has a rich phase diagram, which has been established in the present paper. In addition to the spin-reorientation temperatures (described in the phase diagram), the system also has a Curie temperature that changes from zero (paramagnetic) at $x=0$ up to 920 K (hard magnet) at $x=5$. However, at $x_c \sim 1.9$ we found a sudden increase in T_C, and this feature is explained in terms of percolation theory. More precisely, we ratify this hypothesis by means of determination of critical exponent of the equation $(T_C - T_C^*) \propto (x - x_c)^\beta$, where we could obtain $\beta = 0.43(2)$ (the theoretical value for a 3D lattice is 0.41). We conclude therefore that the percolation process dominates the main magnetic behavior of these materials, since it is responsible for the fast increasing of the Curie temperature, from a paramagnetic compound ($PrNi_5$) up to a hard magnet ($PrCo_5$).

Concerning the advantage of the magnetocrystalline anisotropy on the magnetocaloric properties, we found that for $x \lesssim 2.15$ the magnetic entropy change peak related to the spin-reorientation merges with that around T_C, leading therefore to a large full width at half maximum δT_{FWHM}, for instance, $\delta T_{FWHM}=160$ K for $x=2.15$. Thereby RCP reaches appreciable values which are comparable to the Gd ones.

ACKNOWLEDGMENTS

The authors thank FCT for the VSM equipment (Grant No. REEQ/1126/2001) and the project POCI/CTM/61284/2004. D.L.R. thanks CICECO and FCT (Grant No. SFRH/BPD/41927/2007) for the grant.

---

*dlrocco@fis.ua.pt

[1] W. Wallace, R. Craig, H. Gupta, S. Hirosawa, A. Pedziwiatr, E. Oswald, and E. Schwab, IEEE Trans. Magn. **20**, 1599 (1984).

[2] E. M. T. Velu, R. T. Obermyer, S. G. Sankar, and W. E. Wallace, IEEE Trans. Magn. **25**, 3779 (1989).

[3] P. J. von Ranke, V. K. Pecharsky, K. A. Gschneidner, and B. J. Korte, Phys. Rev. B **58**, 14436 (1998).

[4] A. S. Ermolenko, A. V. K., and A. F. Rozhda, IEEE Trans. Magn. **13**, 1339 (1977).

[5] Y. C. Chuang, C. H. Wu, S. C. Chang, and T. C. Li, J. Less Common Met. **97**, 245 (1984).

[6] A. V. Andreyev, A. V. Deryagin, and S. M. Zadvorkin, Phys. Met. Metallogr. **60**, 96 (1985).

[7] H. H. Van Mal, K. H. J. Buschow, and F. A. Kuijpers, J. Less Common Met. **32**, 289 (1973).

[8] A. S. Ermolenko, IEEE Trans. Magn. **15**, 1765 (1979).

[9] P. J. von Ranke, M. A. Mota, D. F. Grangeia, A. M. G. Carvalho, F. C. G. Gandra, A. A. Coelho, A. Caldas, N. A. de Oliveira, and S. Gama, Phys. Rev. B **70**, 134428 (2004).

[10] Y. C. Chuang, C. H. Wu, and Y. C. Chang, J. Less Common Met. **84**, 201 (1982).

[11] N. Coroian, V. Klosek, and O. Isnard, J. Alloys Compd. **427**, 5

(2007).

[12] M. R. Ibarra, L. Morellon, P. A. Algarabel, and O. Moze, Phys. Rev. B **44**, 9368 (1991).

[13] D. Stauffer and A. Aharony, *Introduction to Percolation Theory* (Taylor and Francis, London, 1992).

[14] A. M. L. Lopes, J. P. Araújo, J. J. Ramasco, E. Rita, V. S. Amaral, J. G. Correia, and R. Suryanarayanan, Phys. Rev. B **73**, 100408(R) (2006).

[15] C. Zlotea and O. Isnard, J. Alloys Compd. **346**, 29 (2002).

[16] K. H. J. Buschow and M. Brouha, J. Appl. Phys. **47**, 1653 (1976).

[17] M. Fahnle and H. Oesterreicher, Phys. Rev. B **29**, 2793 (1984).

[18] M. Fahnle and H. Oesterreicher, Phys. Rev. B **27**, 5586 (1983).

[19] A. J. Bray, Phys. Rev. Lett. **59**, 586 (1987).

[20] M. B. Salamon, P. Lin, and S. H. Chun, Phys. Rev. Lett. **88**, 197203 (2002).

[21] C. Magen, P. A. Algarabel, L. Morellon, J. P. Araujo, C. Ritter, M. R. Ibarra, A. M. Pereira, and J. B. Sousa, Phys. Rev. Lett. **96**, 167201 (2006).

[22] V. K. Pecharsky and K. A. Gschneidner, J. Appl. Phys. **86**, 565 (1999).

[23] K. A. Gschneidner and V. K. Pecharsky, Annu. Rev. Mater. Sci. **30**, 387 (2000).