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High refrigerant capacity of $PrNi_{5-x}Co_x$ magnetic compounds exploiting its spin reorientation and magnetic transition over a wide temperature zone

D L Rocco[1], J S Amaral[1], J V Leitão[1], V S Amaral[1], M S Reis[1], Soma Das[1], R P Fernandes[2], J P Araújo[3], A M Pereira[3] , P B Tavares[4], Nuno V Martins[4] and A A Coelho[5]

[1] Departamento de Física and CICECO, Universidade de Aveiro, 3810-193 Aveiro, Portugal
[2] Technische Universität Hamburg-Harburg, Institut für Keramische Hochleistungswerkstoffe, Hamburg, Germany
[3] IFIMUP, Departamento de Física, Universidade do Porto, 4169-007 Porto, Portugal
[4] Departamento de Química and CQ-VR, Universidade de Trás-os-Montes e Alto Douro, 5009-911 Vila Real, Portugal
[5] Instituto de Física Gleb Wataghin, Universidade Estadual de Campinas - UNICAMP,Campinas, S. Paulo, Brasil

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Abstract
The ferromagnetically coupled cobalt ion is observed to create a magnetocrystalline anisotropy in the $PrNi_{5-x}Co_x$ structure above a critical composition of $x = 2$. The competition of the anisotropy energies between Co and Pr sublattices gives rise to a spin reorientation (SR) phenomenon in $PrNi_{5-x}Co_x$ compounds at a low temperature (~150 K) which is then followed by a magnetic transition at a higher temperature. Co-doping has a strong influence on the Curie temperature, changing it from ~60 K ($x = 1.95$) to ~537 K ($x = 3$). The magnetic entropy change is associated with SR as well as a magnetic transition, and correspondingly a large full width at half maximum (δT_{FWHM}) is obtained for this series of compounds. For example, the $PrNi_{2.85}Co_{2.15}$ compound presents $\delta T_{FWHM} = 166$ K at a 1 T field. This series therefore has an appreciable relative cooling power, which makes this material a suitable magnetic refrigerant over a large temperature span.

1. Introduction

Magnetic refrigeration based on the magnetocaloric effect (MCE) has attracted much research interest due to its potential advantage of being environment-friendly over gas refrigeration [1, 2]. When a material is magnetized in an applied magnetic field, the entropy associated with the magnetic degrees of freedom (S) is changed as the field changes the magnetic order of the material. Under adiabatic conditions, ΔS must be compensated by an equal but opposite change in the entropy associated with the lattice, resulting in a change in the temperature of the material. This temperature change, ΔT, is usually called the MCE. It is related to the magnetic properties of the material through the thermodynamic Maxwell relation $(\partial S/\partial H)_T = (\partial M/\partial T)_H$. The origin of the MCE in many materials has been explained and its practical use to achieve low temperature is being anticipated. The first order magnetic transition coupled to a structural one (or volume cell variation) such as $Gd_5(Si_xGe_{1-x})_2$ [3], MnAs and its derivatives [4, 5] and $La(Fe,Si)_{13}H_y$ [6] is advantageous to a potential magnetic refrigerant material. However, $PrNi_{5-x}Co_x$ compounds have another advantage, namely, the spontaneous spin-orientation transition, which generally occurs in $R(Co_{1-x}Ni_x)_5$ with R = Pr, Nd, Tb, Dy, Ho [7]. The $PrNi_5$ compound has been successfully used for cooling at very low temperatures through the adiabatic demagnetization process [2]. For intermediate concentrations, some authors found for the

$R\mathrm{Ni}_{5-x}\mathrm{Co}_x$ compounds (R: rare earth), with the increase in the Co content: (i) a monotonic increase in the T_C and M_S, (ii) an abrupt change in T_C and M_S near the Co content $x \sim 2.0$ and (iii) a discontinuity in the lattice parameters also around $x \sim 2.0$ [7–10]. In this paper, therefore, we prepared samples of the $\mathrm{PrNi}_{5-x}\mathrm{Co}_x$ series, corresponding to the special compositional region in the range $1.95 \leqslant x \leqslant 3$ in order to study a detailed analysis of its magnetic and magnetocaloric properties and to control the critical temperature around room temperature. The particular choice of praseodymium was guided by its wide temperature span of the Curie temperature up to ~900 K for PrCo_5 [7].

2. Experiment

$\mathrm{PrNi}_{5-x}\mathrm{Co}_x$ (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 synthesized by arc melting under a purified argon atmosphere, starting from the stoichiometric 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 seven days, with a subsequent quench in liquid nitrogen. The weight loss was <0.5%. The energy dispersive x-ray spectroscopy (EDS) technique was used to confirm the homogeneity and the stoichiometry of the sample, and we therefore got single phase samples with the composition of the elements within 6% of the nominal one. The phase purity and crystal structure of the sample were studied by powder x-ray diffraction using a multichannel detector x-ray diffractometer from Phillips with Cu K_α radiation. Rietveld analysis was carried out to confirm that the samples are single phase and crystallize in the hexagonal $CaCu_5$ ($P6/mmm$) type structure. The lattice parameters (at 300 K) are in good agreement with the values found by Chuang *et al* [9] and Andreyev *et al* [7] for poly- and single crystals, respectively. Magnetization as a function of the magnetic field and the temperature was carried out in two vibrating sample magnetometers (VSMs), one for a low temperature (up to 300 K) and another for measurements at a high temperature (300–900 K).

3. Results and discussion

The total magnetization of the polycrystalline $\mathrm{PrNi}_{5-x}\mathrm{Co}_x$ series of samples is measured in the direction of the external field axis. The magnetization measured at a field of 100 Oe, normalized at its maximum value, when plotted as a function of the temperature (figure 1), clearly showed three distinct temperature points, namely, the Curie temperature (T_C), which is then followed by two inflection points at low temperatures of the curve, T_{SR2} and T_{SR1}. The Co content influenced the Curie temperature strongly, changing it from ~60 K for $x \sim 1.95$ up to ~537 K for $x \sim 3.00$. However, the low temperature inflection points (T_{SR1} and T_{SR2}) showed an almost constant value independent of Co-doping. As already discussed [7, 11], the magnetic moment in these $R(\mathrm{Co}_{1-x}\mathrm{Ni}_x)_5$ compounds above a certain temperature (T_{SR2}) is in the direction of the hexagonal c-axis (because of the higher anisotropy of the Co

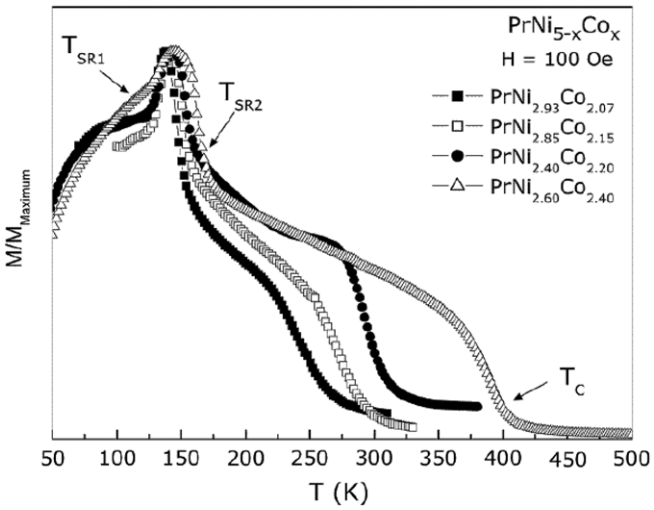

Figure 1. Normalized magnetization as a function of temperature for four samples of the series.

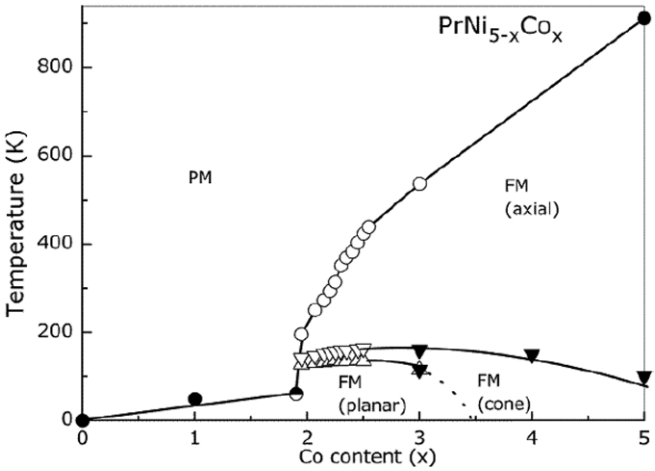

Figure 2. Magnetic phase diagram of the $\mathrm{PrNi}_{5-x}\mathrm{Co}_x$ system. Open symbols—this work, closed symbols—Andreyev *et al* [7] and half filled symbols—estimation. ○/●—Curie temperature, △/▲—T_{SR1} and ▽/▼—T_{SR2}, respectively. PM and FM stands for paramagnetic and ferromagnetic, respectively.

sublattice) whereas, below a particular temperature (T_{SR1}), it becomes in the basal plane (a–b) perpendicular to the c-axis (coming from the anisotropy of the Pr sublattice), and in between, a cone of the easy axes appears where the spin reorientation (SR) is caused by the strong competition between the magnetocrystalline anisotropies of both the 4f and 3d sublattices. Figure 2 presents the magnetic phase diagram for the $\mathrm{PrNi}_{5-x}\mathrm{Co}_x$ series in the full composition range. A detailed description of this diagram will be published elsewhere.

In order to calculate the magnetic entropy change (ΔS), we have measured the magnetization curves at various temperatures up to an applied field of 1 T (the value suitable for the refrigeration application) [12]. The magnetic entropy change ΔS, according to classical thermodynamic theory, can be written as

$$\Delta S(T, H) = \int_0^H \left(\frac{\partial M}{\partial T}\right)_H \mathrm{d}H. \qquad (1a)$$

One method to evaluate the magnetic entropy change (ΔS) is to use isothermal magnetization measurements. For small discrete fields and temperature intervals, ΔS may be approximated from equation (1*a*) by

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

where M_i and M_{i+1} are the experimental values of magnetization at temperatures T_i and T_{i+1}, respectively, under an applied magnetic field H_i. The magnetic entropy change ΔS obtained from equation (1*b*) (figure 3) exhibits a negative peak at T_{SR1} corresponding to plane-to-cone SR whereas at T_{SR2}, ΔS shows a positive peak when the system undergoes a cone-to-axis SR. Finally a high temperature positive peak of ΔS is obtained related to ferro–para transition at T_C. The striking feature obtained for all the samples of the present series is that the magnetic entropy change ΔS shows its maximum value at T_{SR2} rather than at T_C. This is ascribed to the sharper change in magnetization at the SR from the cone to the axis rather than that at the ferro–para transition. Also, the SR processes are accompanied by the magnetostriction effect along the *c*-axis [7, 13], increasing therefore the magnetocaloric potential. This behaviour was already found in the $DyAl_2$ compound both from theoretical calculation and experimental view [14].

As seen from figure 3, from $PrNi_2Co_3$ ($x = 3$) down to $x \sim 2.15$, we have separated magnetic entropy change peaks at T_C and T_{SR2}. The onset concentration for the merged peaks occurs at $x \sim 2.15$, and as a consequence, it drastically increases the full width at half maximum δT_{FWHM} of the entropy curves at $x \sim 2.15$. Figure 4(*a*) summarizes these behaviours. Above $x \sim 2.15$, ΔS peaks at T_C and T_{SR2} are separated and we get an almost constant δT_{FWHM} up to the Co concentration $x = 3.0$; a typical value for δT_{FWHM} for the $x \sim 3.0$ sample is 88 K at T_C (537 K) and 34 K at T_{SR2} (202 K). Below $x \sim 2.15$, we get a large value of δT_{FWHM} due to the merged peaks (from spin reorientation and ferro–para transition). The magnetic entropy change ΔS_{max} around the SR at T_{SR2} of this series of samples shows a strong compositional dependence of cobalt giving a maximum at $x \sim 2.5$ (figure 4(*b*)) while ΔS_{max} around T_C remains approximately constant through Co changes. The relative cooling power (RCP), defined as ΔS_{max} times δT_{FWHM}, is quite large for this series, in spite of this low value of the magnetic field change (1 T). Because of a high value of δT_{FWHM} coming from the merged peaks of ΔS, the RCP value obtained is also high; say 30 J Kg^{-1} (for the $x = 2.07$ sample), whereas that for metallic Gd is 60 J Kg^{-1} at the same conditions [2]. It is worth noting that the RCP of Gd is only 2 times larger than $PrNi_{5-x}Co_x$ while the Gd maximum ΔS_{max} is 12 times higher.

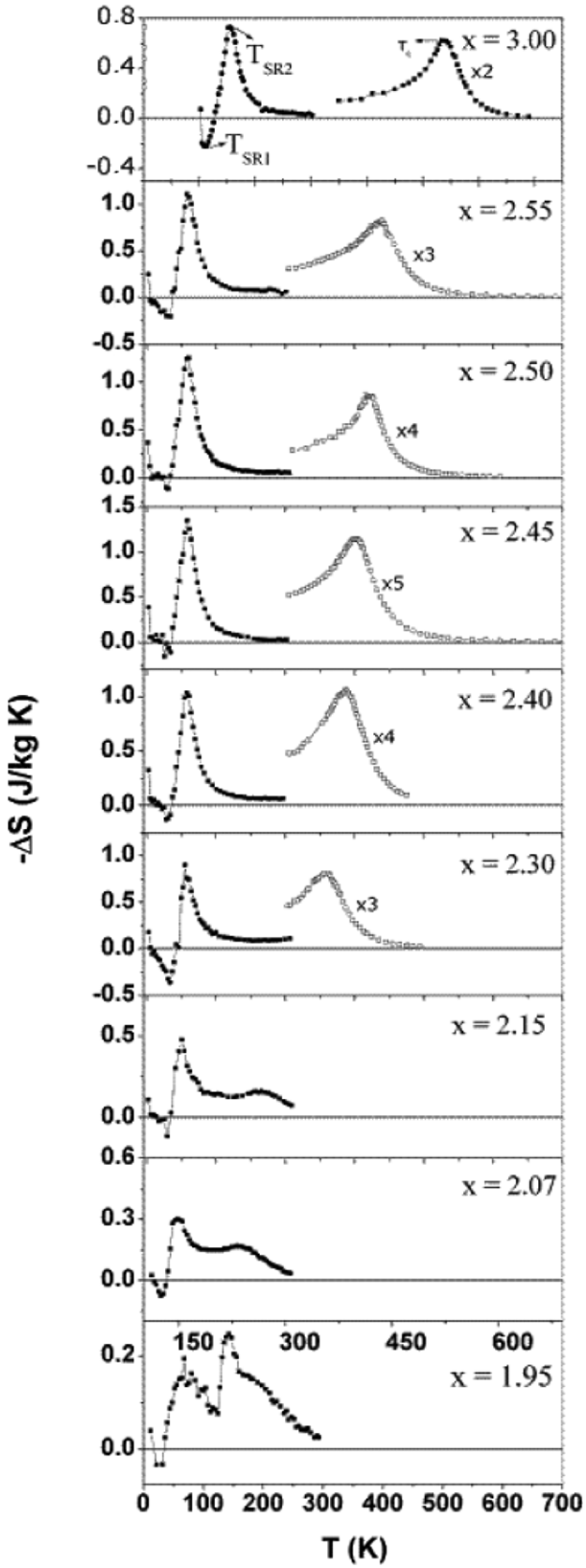

Figure 3. Temperature dependence of the magnetic entropy change obtained from the isothermal magnetization curves, for all the samples prepared. The peaks are associated with the SR process (around T_{SR1} and T_{SR2}) and Curie temperature (T_C). Note the high value of δT_{FWHM} of the peak around T_C (for a higher Co concentration). On decreasing the Co content the peaks around T_{SR2} and T_C merge increasing the δT_{FWHM}.

4. Conclusion

This study therefore opens up the possibility for a good magnetic refrigerant by exploiting the SR phenomena of the magnetic materials, already claimed by theoretical work [14].

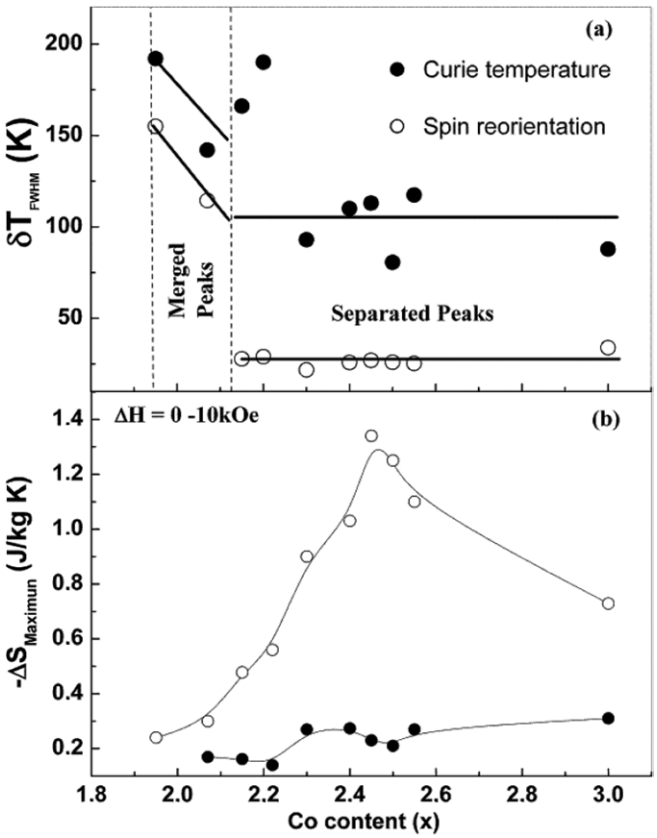

Figure 4. (*a*) Full width at half maximum around T_C and T_{SR2} peaks. Below $x = 2.15$ those peaks merge, increasing the δT_{FWHM}. (*b*) Maximum magnetic entropy change around T_C and T_{SR2}.

The $PrNi_{5-x}Co_x$ series, in the special concentration range of $1.95 \leqslant x \leqslant 3$, shows a large change in the Curie temperature from ~60 K for $x = 1.95$ to ~537 K for $x \sim 3$. Because of its reaching SR at a low temperature, it gives a wide δT_{FWHM} and therefore a high RCP although ΔS_{max} is nominal. Also a wide range of the working temperature zone is achieved with this series.

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