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Differential scanning calorimetry experiments in RCo_2

J. Herrero-Albillos[a,*], F. Casanova[b], F. Bartolomé[a], L.M. García[a], A. Labarta[b], X. Batlle[b]

[a] *Instituto de Ciencia de Materiales de Aragón, CSIC-Universidad de Zaragoza, Pedro Cerbuna 12, 50009 Zaragoza, Spain*
[b] *Departament Física Fonamental, Universitat de Barcelona, Diagonal 647, 08028 Barcelona, Catalonia, Spain*

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Abstract

Differential scanning calorimetry experiments have been performed under magnetic field in RCo_2 Laves phases compounds (R = Pr, Nd, Tb, Dy, Ho, and Er) in order to clarify the nature of their ordering transitions. A significant controversy is present in previous literature about the character of $PrCo_2$ and $NdCo_2$ ferromagnetic transitions. The calorimetric curves show without ambiguity that they are second-order transitions. For the compounds showing a first-order transition, enthalpy and entropy changes have been obtained. $ErCo_2$ calorimetric curves show a fine peak structure that can be related with the anisotropy of the coexistence curve.

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Keywords: Magnetocaloric effect; Rare-earth–transition metal compounds; Anisotropy—magnetic; Phase transitions

Cobalt Laves phases, RCo_2, have been long studied for their interesting magnetic properties such as the metamagnetic character of the cobalt sublattice [1] or its magnetocaloric properties [2]. When formed with non-magnetic R elements, RCo_2 are exchange-enhanced paramagnets. The Co moment can be induced in those compounds by applying very high magnetic fields (>70 T for YCo_2), giving rise to a metamagnetic transition in Co to a ferromagnetic state. In contrast, in the RCo_2 compounds formed with a magnetic rare earth, the internal field is able to induce the Co moment and to polarize it. Due to the third Hund's rule and the intersublattice exchange, the coupling between the R and Co moments is ferrimagnetic in compounds formed with a heavy rare earth (Gd, Tb, Dy, Ho, Er) and ferromagnetic in those formed with a light rare earth (Pr, Nd, Sm). For some compounds the formation of the Co magnetic moment leads to a first-order transition at the R ordering temperature.

Since the 1960s, RCo_2 ordering phase transitions were reported to be first order in the case of R = Dy, Ho, and Er, and second order for all the other compounds (see Ref. [1] and references therein). However, recent perturbed angular correlation experiments carried out by Forker et al. [3] indicate a first-order character of the transition in $NdCo_2$ and $PrCo_2$. X-ray diffraction, transport properties, or magnetization measurements, among other experiments, are not fully conclusive in determining the order of the transition in $NdCo_2$ and $PrCo_2$. Moreover, first theoretical works studying the nature of the transitions in these compounds predicted a first-order transition for $NdCo_2$ and $PrCo_2$ [4]. On the other hand, more advanced models predicted the

*Corresponding author. Tel.: +34 976 762 692; fax: +34 976 761 229.
E-mail address: julia.herrero@unizar.es (J. Herrero-Albillos).

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occurrence of second-order transitions in these compounds [5].

In order to clarify this disagreement, we have performed differential scanning calorimetry (DSC) experiments at various fields (0–5 T) scanning the temperature from 15 to 300 K in six polycrystalline samples of the series: R = Pr, Nd, Tb, Dy, Ho, and Er. In DSC, the heat flow is directly measured. Consequently, this technique is one of the most suitable to study the nature of a phase transition, giving irrefutable proof of the order of the transition in $NdCo_2$ and $PrCo_2$. For first-order transitions, the integration of the DSC signal yields the transition latent heat, while in second-order transitions the signal reflects the continuous change of entropy through the transition. A detailed description of the experimental setup can be found in Ref. [6].

Samples were prepared by melting the pure elements in an induction furnace under Ar atmosphere and were annealed at 850 °C for a week. X-ray diffraction analysis was performed to check if samples were single phase. Magnetization curves carried out in a SQUID magnetometer are fully consistent with those reported in the literature. For the Laves phases formed with a light rare earth, $PrCo_2$ and $NdCo_2$, the ferromagnetic transitions occur at 40 and 98 K, respectively. For those compounds formed with heavy rare earths, $TbCo_2$, $DyCo_2$, $HoCo_2$, and $ErCo_2$, the ordering transitions to the ferrimagnetic state are at 231, 138, 78, and 34 K. We have also identified the first-order spin reorientation transition (SRT) in $NdCo_2$, in which the easy axis changes from [1 0 0] at low temperature to [1 1 0] above 42 K.

As can be seen in Fig. 1, DSC data for $NdCo_2$ and $PrCo_2$ at zero field clearly reveal the second-order nature of the ferromagnetic transition: a λ-type shape is observed. Calorimetric curves for $TbCo_2$ also show the second-order character of its ferrimagnetic transition, as expected. In the three compounds, the small temperature shift between the cooling and heating curves originates from the different scan rate of the two processes.

On the other hand, $HoCo_2$ and $ErCo_2$ DSC data distinctly exhibit the first-order nature of the transitions. The curves show the expected sharp shape, thermal hysteresis, and variation of the critical temperature with the applied field ($\sim 3.4\,K/T$ for $HoCo_2$ and $\sim 2\,K/T$ for $ErCo_2$). In addition, a broadening of the peaks is observed as the applied field is increased. The whole set of curves recorded on cooling and heating in $ErCo_2$ for different applied fields (0–5 T) is shown in Fig. 2.

$DyCo_2$ shows a wide peak at zero field and no thermal hysteresis is observed. Nevertheless, the characteristic field dependence of the critical temperature for a first-order transition is observed in the calorimetric curves measured at different fields ($\sim 3.5\,K/T$). Additionally, the peak broadens with the application of a small field (~ 0.5 T), being almost inappreciable at 5 T. This weak first-order-transition behavior has already been reported [1].

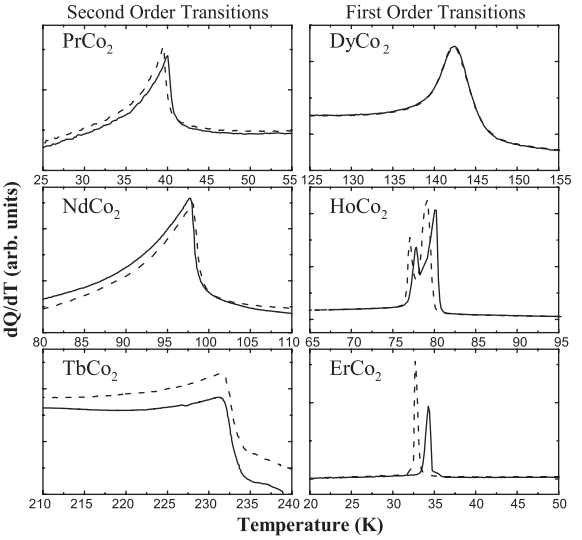

Fig. 1. DSC measurements on heating (solid lines) and cooling (dashed lines) at zero field for $PrCo_2$, $NdCo_2$, $TbCo_2$, $DyCo_2$, $HoCo_2$, and $ErCo_2$.

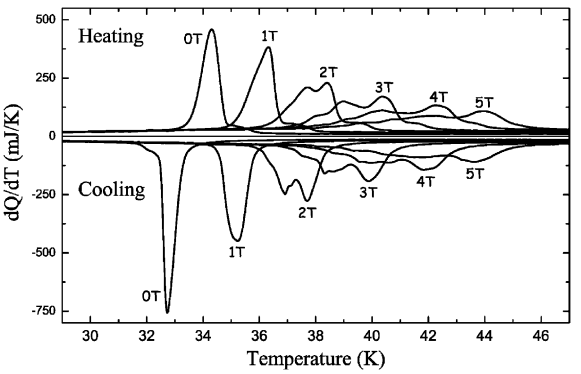

Fig. 2. Calorimetric curves on heating and cooling for $ErCo_2$ under different applied fields.

Enthalpy (ΔH) and entropy changes (ΔS) at the first-order transitions (in $DyCo_2$, $HoCo_2$, and $ErCo_2$) have been determined for different applied fields. ΔS values are in agreement with those reported in the literature for the three compounds [2]. ΔH and ΔS values for zero field and the maximum applied field are presented in Table 1. ΔH and ΔS decrease as the field increases (i.e. the critical temperature increases) in all the compounds for both heating and cooling.

Calorimetric curves across the $NdCo_2$ SRT have also been measured as shown in Fig. 3. $NdCo_2$ SRT data also show all the characteristics reported for first-order transitions. ΔH and ΔS are also presented in Table 1.

As it is shown in Fig. 2, the calorimetric curves in polycrystalline $ErCo_2$ show a fine peak structure near

Table 1
Enthalpy ($J\,kg^{-1}$) and entropy changes ($J\,kg^{-1}\,K^{-1}$) in the ferrimagnetic first-order transition for $ErCo_2$, $HoCo_2$, $DyCo_2$, and the first-order spin reorientation in $NdCo_2$

	$ErCo_2$		$HoCo_2$		$DyCo_2$		$NdCo_2^{SRT}$	
	0T	5T	0T	5T	0T	1.5 T	0T	1T
$\Delta H_{heating}$	1526	1264	1580	852	1215	586	130	73
$\Delta H_{cooling}$	−1684	−1320	−1612	−890	−1221	−612	−148	−86
$\Delta S_{heating}$	43.3	29.1	20.0	8.9	8.5	4.0	3.1	1.6
$\Delta S_{cooling}$	−49.0	−32.4	−20.5	−9.2	−8.6	−4.2	−3.5	−1.9

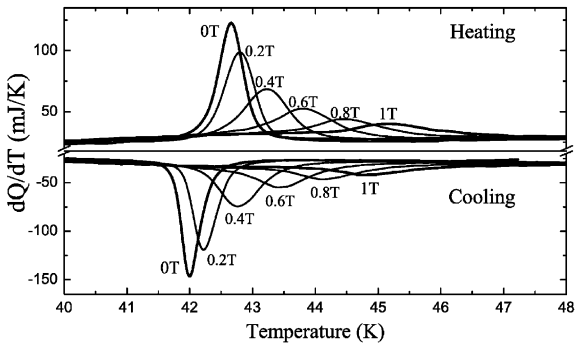

Fig. 3. Calorimetric curves on heating and cooling for $NdCo_2$ at the SRT under different applied fields.

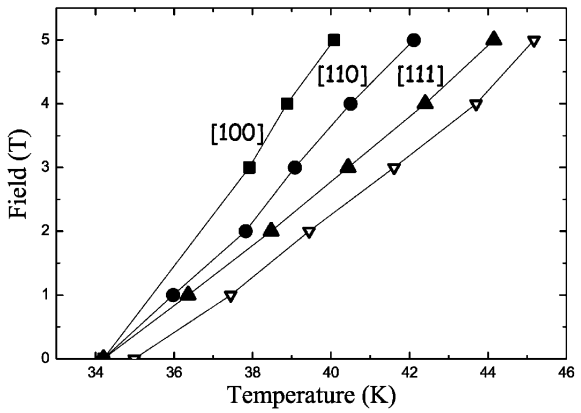

Fig. 4. Peak positions of the calorimetric curves (heating) in the polycrystalline sample $ErCo_2$. The three main peaks are related to the three crystallographic directions in $ErCo_2$.

the ferrimagnetic transition. At zero field a main peak is observed together with a minor one (located at a higher temperature for the heating curve). Under an applied magnetic field, the main peak splits into three distinct peaks, which gradually move away from each other and broaden as the field is increased. At the same time, the minor peak shifts to higher temperatures but remains at a constant ΔT with respect to the highest peak. Each calorimetric curve has been fitted to the sum of four pseudo-Voigt functions in order to determine the peak positions as a function of the applied field. The results for the heating process are shown in Fig. 4.

Magnetization and magnetoresistance measurements on single crystal $ErCo_2$ reveal the existence of an anisotropy in the coexistence curve (H_c–T_c) with respect to the relative direction between the applied field and the crystallographic directions. The agreement between the temperatures deduced from DSC and those from Ref. [7] is remarkable. In view of that, we interpret the three main peaks of DSC data as due to the three crystallographic directions [1 0 0], [1 1 0], and [1 1 1]. That is to say, for a fixed magnetic field, the sample grains have different ordering temperatures depending on the relative orientation with respect to the magnetic field. Therefore, in the polycrystalline sample, three transition temperatures are observed.

Conversely, in $HoCo_2$ two well-defined peaks are present in the calorimetric curves at zero field (see Fig. 1). Despite the fact that ΔT between the peaks remains constant as the field is increased, the peaks overlap at high fields (3–5 T) due to their broadening. This behavior is in agreement with the lack of anisotropy of the coexistence curve in $HoCo_2$ described in Ref. [8]. The origin of these two peaks as well as the minor peak in $ErCo_2$ is not yet fully understood, although the microstructure of the sample may be at the origin of this phenomenon. Indeed, a noticeable dependence of T_c on the grain size distribution has been recently shown in other first-order magnetocaloric compounds [9].

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