

Nature and entropy content of the ordering transitions in $R\text{Co}_2$

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(Received 28 July 2005; revised manuscript received 24 January 2006; published 11 April 2006)

Differential scanning calorimetry experiments have been performed under magnetic field in $R\text{Co}_2$ Laves phases compounds ($R=\text{Pr}$, Nd , Tb , Dy , Ho , and Er). The thermodynamical nature of the ferromagnetic transitions in PrCo_2 and NdCo_2 is clarified, after the controversy present in the literature about the character of their ordering transitions. The magnetocaloric effect in the compounds showing a first-order magnetostructural transition ($R=\text{Dy}$, Ho , and Er) is characterized. The latent heat, L , and the entropy change at the transition, ΔS , have been studied by inducing the transition sweeping the temperature at a constant field and sweeping the field at a constant temperature. Results from calorimetric data show that L is essentially temperature independent, suggesting that the first order transitions in $R\text{Co}_2$ are dominated by the structural effects. The magnetocaloric effect has been also characterized from magnetization data and the results are in excellent agreement with those from calorimetric data. However, the corresponding values of ΔS for isothermal and isofield experiments differ significantly. We interpret the differences in terms of the broadness of the transitions and prove that the various ΔS values reported in literature for first-order transitions are not always directly comparable.

DOI: [10.1103/PhysRevB.73.134410](https://doi.org/10.1103/PhysRevB.73.134410)

PACS number(s): 75.30.Sg, 65.40.Gr, 71.20.Lp

I. INTRODUCTION

Cobalt Laves phases, $R\text{Co}_2$, and the metamagnetic character of its cobalt sublattice have evoked a far reaching interest since the 1960s (for recent reviews on $R\text{Co}_2$ compounds, see Refs. 1 and 2). In the compounds where R is a nonmagnetic rare earth, the Co moment can be induced by applying very high magnetic fields (>70 T for YCo_2),³ giving rise to a metamagnetic transition. However, in the $R\text{Co}_2$ compounds formed with a magnetic rare earth, the internal field is able to induce and polarize the cobalt moment. Due to the intersublattice exchange and third Hund's rule, the rare earth and cobalt moments are coupled parallel in compounds formed with light rare earths (i.e., $R\text{Co}_2$ with $R=\text{Pr}$, Nd , and Sm are ferromagnets) and antiparallel in those formed with heavy rare earths (i.e., $R\text{Co}_2$ with $R=\text{Gd}$, Tb , Dy , Ho , and Er are ferrimagnetic compounds).^{4,5}

In DyCo_2 , HoCo_2 , and ErCo_2 compounds, the magnetic ordering to the ferrimagnetic state is coupled to a structural change, leading to a first-order transition at the critical temperature. The high values of the magnetic moment for $R=\text{Dy}$, Ho , and Er in $R\text{Co}_2$ compounds⁴⁻⁶ give rise to a remarkable entropy change (ΔS) at their first-order transitions, turning this family of compounds into potential candidates for magnetic cooling in the 30–150 K temperature range. Indeed, the novel trends in high efficiency magnetic refrigeration are based on first-order magnetostructural phase transitions,⁷⁻¹⁰ since magnetization changes abruptly in a narrow temperature range (for reviews on magnetocaloric materials, including $R\text{Co}_2$, see Refs. 11–14).

When characterizing the magnetocaloric effect (MCE) from magnetization measurements, $M(H)$ curves are typically used and, therefore, the explored transitions are induced only by sweeping the magnetic field. On the other

hand, when the MCE is studied by means of calorimetric data, the transitions are generally induced by temperature. Consequently, when comparing the MCE from the two sets of data, care should be taken because different physical quantities are being swept and measured. As first-order magnetic transitions can be induced both by temperature and magnetic field, it is desirable to compare the dependence of the MCE with both parameters and, moreover, to study them under the same conditions, i.e., in the same instrument and measuring the same physical quantities.

We have studied the first-order transition in $R\text{Co}_2$ compounds inducing the transition by sweeping the temperature and the magnetic field by means of magnetization and differential scanning calorimetry (DSC) experiments, and we have found significant differences in ΔS between isothermal and isofield processes. In fact, these discrepancies were already present in the literature for ErCo_2 . Giguere *et al.*¹⁵ reported differences in ΔS values obtained from calorimetric data and those obtained from magnetization measurements and they ascribe the discrepancies to the failure of the approximations used (e.g., they found a 12% difference in the maximum ΔS value at 7 T). Although we have also observed this kind of discrepancies in our data, the agreement between our ΔS values and Giguere's values is poor, probably due to the different quality of the samples. Conversely, our isofield data are in very good agreement with calorimetric data from Wada *et al.*^{16,17} and theoretical calculations from de Oliveira *et al.*,¹⁸ while our isothermal data are in a remarkable agreement with magnetic data from Duc *et al.*^{19,20} In this paper we investigate the origin of the discrepancy in isofield and isothermal data, emphasizing why different ΔS values reported in literature are not always directly comparable.

In addition, we also discuss the nature of the ordering transitions in the $R\text{Co}_2$ series. Most of the experimental work

done on the compounds during the last decades assume that only DyCo_2 , HoCo_2 , and ErCo_2 display a first-order magnetostructural transition, while all the other compounds display second-order transitions.^{1,2,21,22} Nevertheless, the physical properties measured at that time are not fully conclusive in the determination of the nature of the transition in some of the $R\text{Co}_2$ (R =light rare earth) compounds. Indeed, recent perturbed angular correlation experiments by Forker *et al.*,²³ have opened a controversy by claiming a first-order character of the transition in PrCo_2 and NdCo_2 compounds.

There is also a large amount of theoretical work aimed at explaining the nature of the transitions in the whole $R\text{Co}_2$ series and why the magnetic transition changes from second to first-order along the series. In particular, the widely accepted Inoue-Shimizu theory,^{24–26} based on a series expansion of the magnetic free energy, predicts the occurrence of a first-order transition in those $R\text{Co}_2$ compounds with T_c below ~ 200 K. This would predict a first-order character not only for DyCo_2 , HoCo_2 , and ErCo_2 (in general agreement with experimental results), but also for PrCo_2 and NdCo_2 . On the contrary, a more recent work from Khmelevskiy and Mohn,²⁷ which takes into account the evolution of the $R\text{Co}_2$ lattice constant within the lanthanide series, supports the generally assumed second-order character of the transitions in PrCo_2 and NdCo_2 .

In this scenario, an experiment which definitely solves the riddle of the nature of PrCo_2 and NdCo_2 transitions is required. Latent heat is a quantity present only in first-order transitions and, therefore, its presence or absence is a direct proof of the nature of the transition. In a DSC, heat flow is directly measured. Consequently, proper integration of the calorimetric signal yields the latent heat in first-order transitions,²⁸ while in second-order transitions the signal reflects the continuous change of entropy through the transition. Moreover, the study of the transition using DSC under applied magnetic field also discriminates second- from first-order transitions. This technique is thus one of the most suitable to determine the thermodynamic character of a phase transition.^{29,30}

To summarize, we have performed DSC experiments under applied magnetic field in six compounds of the $R\text{Co}_2$ series in order to determine the nature of their ordering transitions and characterize the MCE in these compounds presenting a first-order magnetostructural transition.

The paper is organized as follows: we describe the synthesis and characterization of the samples in Sec. II and the experimental results in Sec. III. We first discuss the nature of the transitions in PrCo_2 and NdCo_2 (Sec. III A), we go on with the study of the shape of the DSC curves in the first-order transitions (Sec. III B) and its relation with the anisotropy of the coexistence curves (Sec. III C). In Sec. III D, we present ΔS , enthalpy change and latent heat values obtained from calorimetric and magnetization data and we discuss the effect of the broadness of the transition when comparing field- and temperature-induced transitions. Finally, in Sec. IV, we summarize the main results obtained.

II. EXPERIMENTAL DETAILS

All the samples are polycrystalline ingots and were prepared by melting the pure elements in an induction furnace

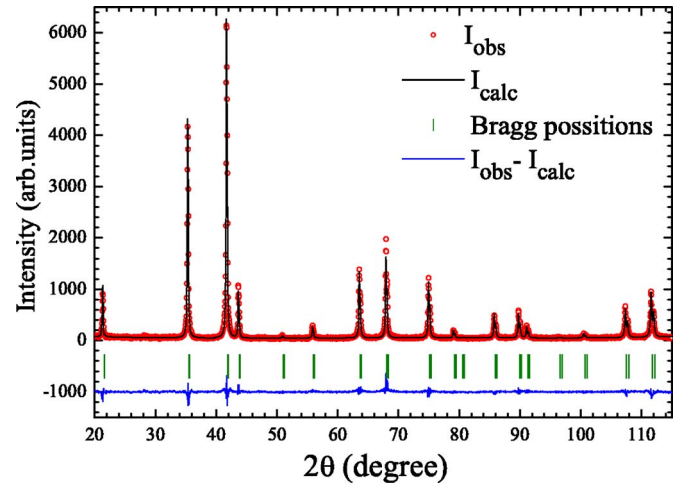


FIG. 1. (Color online) X-ray diffraction data for the ErCo_2 sample. Open circles correspond to experimental data, the solid line is the best fit of the spectra to a single phase, vertical lines show the Bragg positions, and the solid line at the bottom is the difference between experimental and fitted data.

under Ar atmosphere. The resulting ingots were further annealed under Ar atmosphere at 850°C for a week, wrapped in tantalum foil.

X-ray diffraction analysis was performed on powdered samples to check their quality. Rietveld analysis of the diffractograms assured single phase samples with good crystallization. No impurities were found within the 1% accuracy of powder diffraction methods. X-ray diffractogram for ErCo_2 is shown in Fig. 1.

TbCo_2 , HoCo_2 , and ErCo_2 samples were analyzed by scanning electron microscopy. In order to check their homogeneity, energy dispersive spectroscopy was carried out in different areas of the samples. The corresponding main phases were found to have the stoichiometric 1:2 composition with small amounts of oxides due to surface oxidation. Very small areas of the samples were found to have a larger amount of $R_2\text{O}_3$. These rare earth oxides are antiferromagnetic at very low temperatures (<5 K) (Ref. 31) and, therefore, do not contribute to the magnetic behavior of our samples at the temperature range of interest.

The calorimetric measurements were performed in a high-sensitivity DSC specially designed to operate over a temperature range from 10 to 300 K and under magnetic fields up to 5 T. A detailed description of the experimental set up can be found in Ref. 28. Magnetization measurements, $M(T, H)$, from 10 to 300 K and up to 5 T were performed in a SQUID Quantum Design magnetometer. In addition, magnetization measurements in ErCo_2 were completed up to 9 T in a commercial Quantum Design extraction magnetometer. The magnetic ordering at zero field occur at 40 K, 98 K, 231 K, 138 K, 78 K, and 34 K for PrCo_2 , NdCo_2 , TbCo_2 , DyCo_2 , HoCo_2 , and ErCo_2 , respectively. These data are fully consistent with those previously reported.^{1,4,15–18,20,21,32–46}

The $M(T, H)$ surface for the compounds presenting a first-order transition (DyCo_2 , HoCo_2 , and ErCo_2) are shown in Fig. 2. It is worth stressing that, in HoCo_2 and ErCo_2 , transitions are very sharp but DyCo_2 does not show such a char-

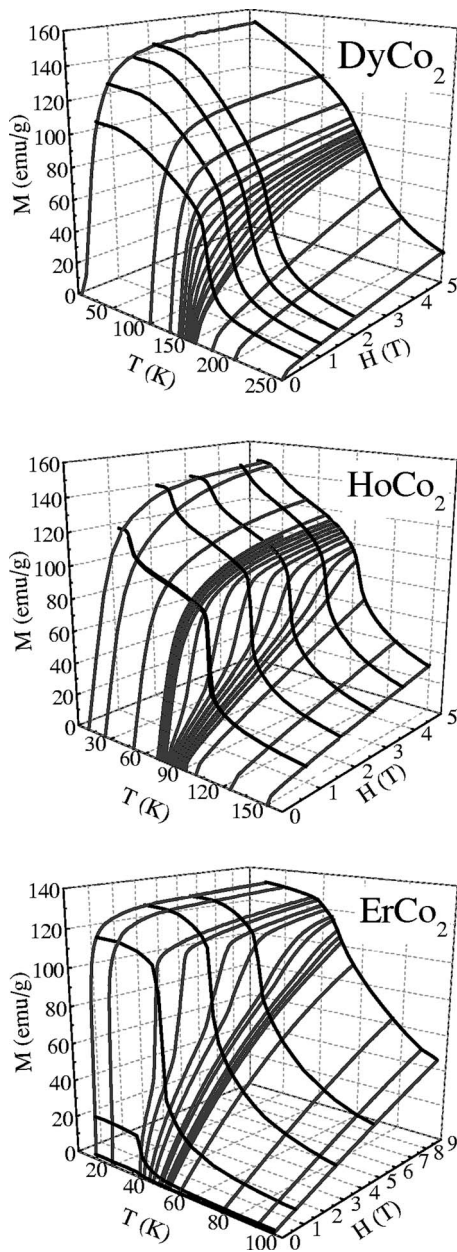


FIG. 2. Temperature and field dependence of magnetization in $DyCo_2$, $HoCo_2$, and $ErCo_2$ compounds.

acteristic shape for a first-order transition. While the transition is still evidenced in the $M(T)$ curves of this compound, the transition region is very difficult to distinguish in the $M(H)$ curves due to the lack of an inflection point.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Character of the magnetic RCo_2 transitions

Among the RCo_2 compounds, $DyCo_2$, $HoCo_2$, and $ErCo_2$ show first-order transitions, but there is a controversy on the nature of the transition in $PrCo_2$ and $NdCo_2$.^{1,2,21-27} In order to clarify this disagreement, we have performed DSC measurements in RCo_2 with $R=Dy, Ho, Er, Tb, Nd,$ and Pr . Figure 3 shows the calorimetric curves obtained from the

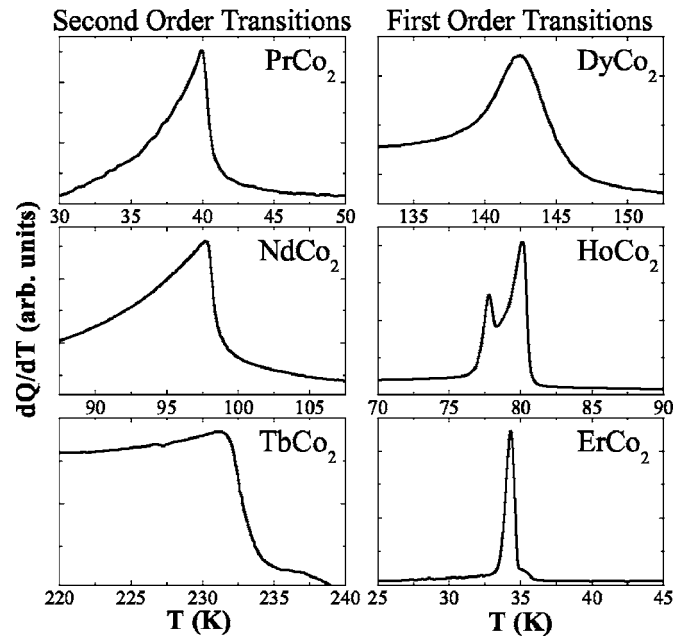


FIG. 3. DSC heating runs at zero field for RCo_2 ($R=Pr, Nd, Tb, Dy, Ho,$ and Er).

experiments performed at zero field inducing the magnetic transition by increasing the temperature. In a previous work⁴⁷ we discussed the second-order nature of the ferromagnetic transition for $NdCo_2$ and $PrCo_2$ from zero field data. In order to clearly establish the nature of these phase transitions, we have performed DSC experiments under applied field in $PrCo_2$ and $NdCo_2$. As can be seen in Fig. 4, the λ -shape transition is only manifested at zero field for both compounds. When a magnetic field is applied, the peak

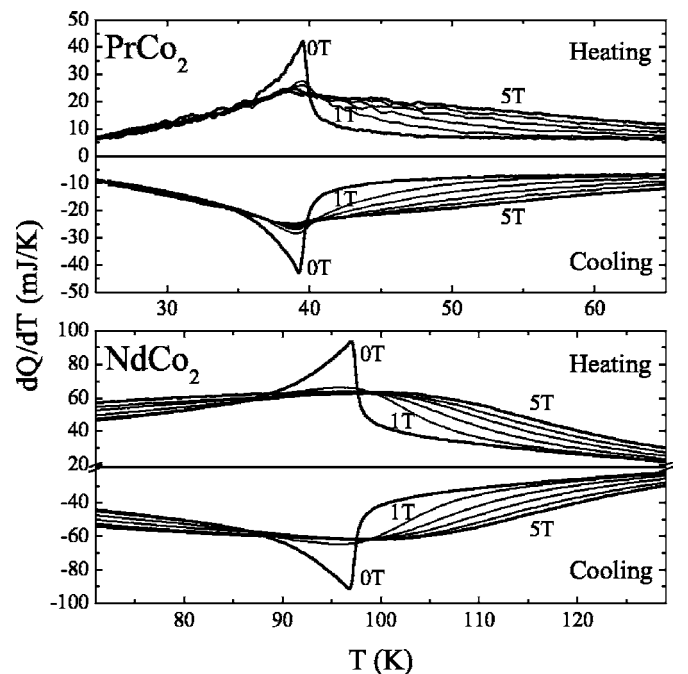


FIG. 4. DSC curves as a function of temperature under selected applied fields ($H=0, 1, 2, 3, 4,$ and 5 T) for $PrCo_2$ and $NdCo_2$.

broadens but the maximum does not shift towards higher temperatures as the field is increased. Furthermore no hysteresis effects have been observed between cooling and heating runs for any of the applied fields.

In view of this, the measurements under applied fields up to 5 T fully rule out the proposed first-order nature of PrCo_2 and NdCo_2 magnetic transitions in Ref. 23. Forker and co-workers based their conclusion on two features of the perturbed angular correlation (PAC) spectra of ^{111}Cd , which should allow us to discriminate the nature of the phase transitions; the variation of the magnetic interaction frequency and the broadening of the PAC lines near T_c .²³ The authors discuss in detail the coexistence of magnetically ordered and disordered phases near T_c in all their samples, leading to a distribution of the ordering temperatures of about 1–2 K (a fact that we have also observed in some of our samples, as we discuss below). The lack of a fine temperature scanning near T_c together with the cited phase-coexistence makes it very difficult to use PAC spectra as a tool to discriminate between first- and second-order phase transitions. In contrast, DSC is the technique of choice when aiming at determine the nature of a transition, especially in those cases hard to discriminate. In our opinion, data shown in the present work unambiguously determine the second-order character of the NdCo_2 and PrCo_2 ordering transitions.

B. Differential scanning calorimetry in first-order transitions for DyCo_2 , HoCo_2 , and ErCo_2

DyCo_2 , HoCo_2 , and ErCo_2 show first-order magnetostructural transitions and therefore present relevant MCE. In order to fully characterize them, we have performed DSC measurements both sweeping the temperature at a constant field [which will be noted as $\text{DSC}_H(T)$ from now on] and sweeping the applied field at a constant temperature [$\text{DSC}_T(H)$].

$\text{DSC}_H(T)$ experiments were carried out at a rate of 3 K/min for heating runs and at 1 K/min for cooling runs. $\text{DSC}_T(H)$ experiments were carried out by increasing and decreasing the field at both 1 T/min and 0.1 T/min. In this way, the transition was induced by the temperature as well as by the magnetic field, at different rates and going from the paramagnetic to the ferrimagnetic region and vice versa. The resulting $\text{DSC}_H(T)$ and $\text{DSC}_T(H)$ signals are shown in Figs. 5 and 6, respectively.

For the three compounds, $\text{DSC}_H(T)$ [$\text{DSC}_T(H)$] curves exhibit the typical field (temperature) dependence of the critical temperature (critical field) for a first-order transition. As it is also expected for a first-order transition, ErCo_2 and HoCo_2 curves show thermal and field hysteresis as well as sharp peaks.

The first-order character of DyCo_2 transition is well established from the above cited dependence of the critical temperature with the applied field, resistivity data⁴⁸ and theoretical calculations.^{24–27} However, $\text{DSC}_{H=0T}(T)$ curves for DyCo_2 show a very wide peak which becomes even broader as soon as a magnetic field is applied (~ 0.3 T). A similar behavior can be observed in the $\text{DSC}_T(H)$ curves for DyCo_2 (see Fig. 6). Moreover, we have not observed any thermal or field hysteresis (in contrast with previous DSC results at zero

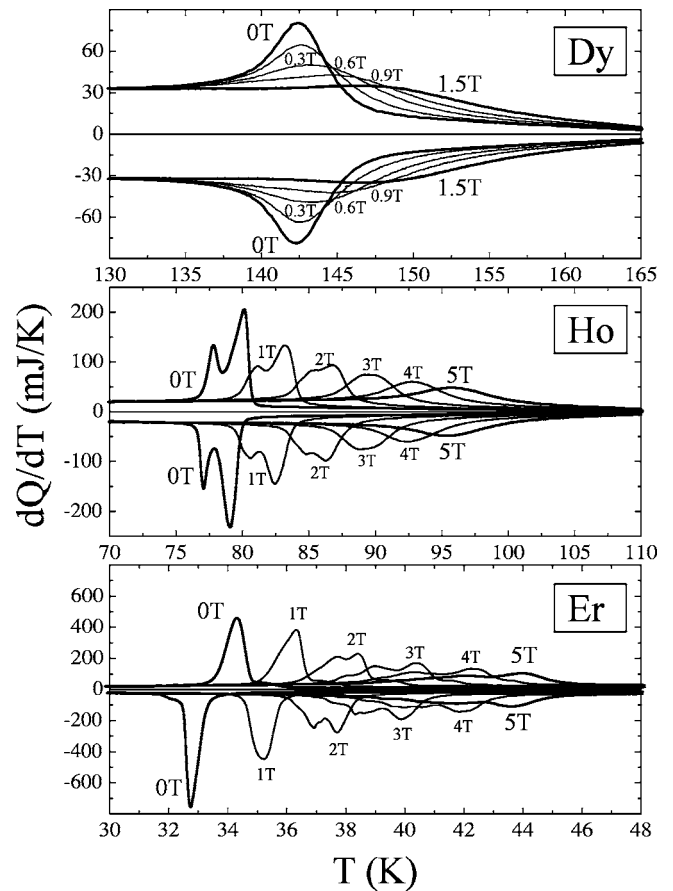


FIG. 5. DSC curves as a function of temperature under selected applied fields for DyCo_2 , HoCo_2 , and ErCo_2 . Positive (negative) signals correspond to the heating (cooling) runs.

field).⁴⁹ This weak first-order behavior could be also seen in the DyCo_2 magnetization surface (see Fig. 2). Previous experimental results^{1,20,33} have suggested that this weak first-order character may originate from the small size of the discontinuity of the free energy derivatives at the transition.

Except for hysteresis effects, no differences in ΔS values at the transition nor in the shape of the curves were observed between cooling and heating measurements for DyCo_2 and HoCo_2 (Fig. 5). For ErCo_2 compound, due to the sharpness of the DSC peaks for the lowest applied fields, the sweeping rate affects the measurement, causing up to 15% difference in the magnitude of MCE. Similarly, no difference between measurements carried out by increasing and decreasing the field was detected in $\text{DSC}_T(H)$ data (Fig. 6), only a finer peak structure was perceived for runs performed at 0.1 T/min. Therefore, in what follows, we shall only refer to the results obtained by heating or by increasing the field.

C. Fine peak structure in the calorimetric curves

All ErCo_2 and HoCo_2 isothermal and isofield calorimetric curves show a peak structure. For the sake of clarity, some of the heating curves for the two compounds are shown again in Fig. 7.

In the ErCo_2 calorimetric curve at zero field, a main peak is observed. Under an applied magnetic field, this peak splits

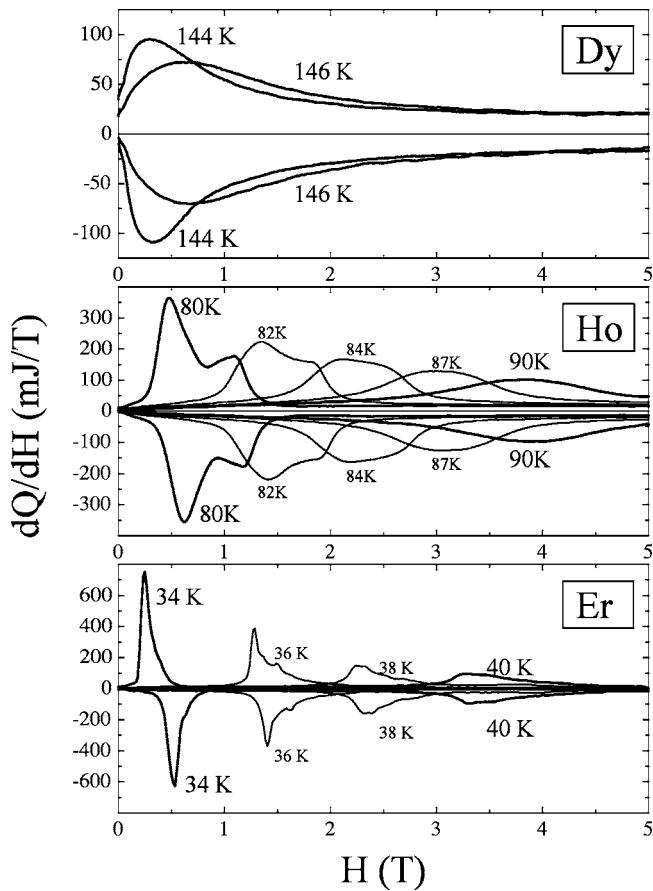


FIG. 6. DSC curves as a function of applied field at selected temperatures for DyCo₂, HoCo₂, and ErCo₂. Positive (negative) signals correspond to measurements carried decreasing (increasing) the applied magnetic field.

into three distinct peaks which gradually move away from each other as the field is increased. A smaller peak in the calorimetric curves can also be observed 1 K above the highest peak, which will be discussed later. At 3 T the four peaks can be fully distinguished, as shown in Fig. 7. Each calorimetric curve has been fitted to the sum of four pseudo-Voigt functions in order to precisely determine the peak positions as a function of the applied field. Results are shown in the inset of Fig. 7.

Magnetization and magnetoresistance measurements on ErCo₂ single crystal by Aleksandryan *et al.*⁵⁰ revealed that, for a fixed magnetic field, T_c depends on the relative orientation of the field with respect to the three crystallographic directions [100], [110], and [111]. Hence, each microcrystal in a polycrystalline sample also has a different ordering temperature depending on its relative orientation with respect to the external magnetic field. Each one contributes to the DSC curve with a peak centered at its own ordering temperature. If the microcrystals are randomly orientated within the sample, DSC curves should present a single wide feature arising from the sum of the contributions of all of them. This is not the case for our calorimetric curves in ErCo₂, as it is shown in Fig. 7, yielding the conclusion that in the process of sample synthesis the crystals have grown preferentially in three crystallographic directions and their equivalent cubic

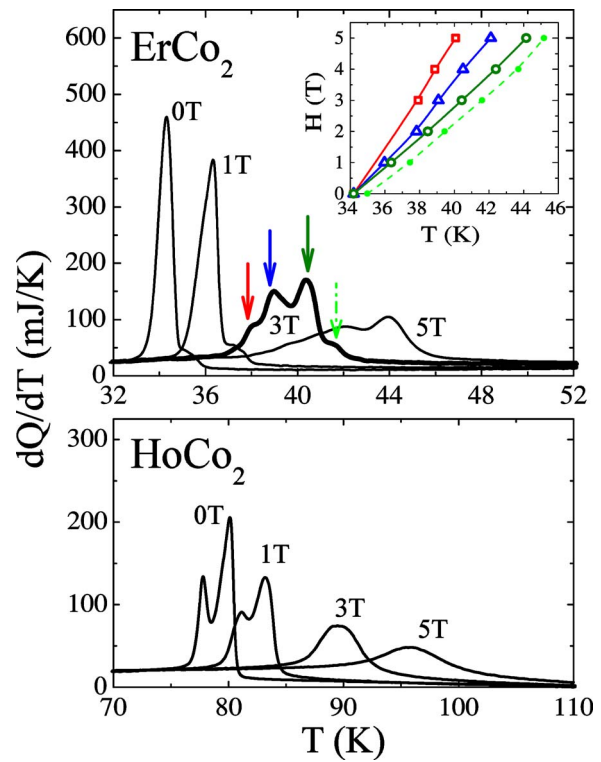


FIG. 7. (Color online) DSC_H(T) heating runs for ErCo₂ and HoCo₂ ($H=0, 1, 3,$ and 5 T). (Inset) Temperature and field dependence of the calorimetric peaks in the polycrystalline sample ErCo₂.

ones. Furthermore, this peak structure can be also observed in the derivative of the magnetization curve shown in Fig. 8. The agreement between the critical temperatures deduced from our DSC data in a polycrystalline sample and those reported in Ref. 50 from a single crystal is remarkable.

The case for HoCo₂ is quite different. The ordering temperature of this compound does not depend on the relative orientation of the crystallographic directions and the field (i.e., the coexistence curve is isotropic with respect to the crystallographic directions⁵¹) and only one peak should be expected in the DSC curves. However, HoCo₂ calorimetric curves show two peaks (Fig. 7), which become broader as

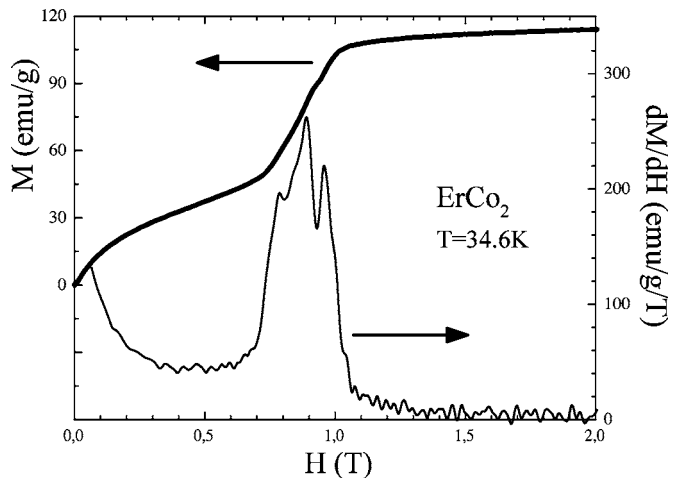


FIG. 8. $M(H)$ and its derivative in ErCo₂ at 34.6 K.

TABLE I. Entropy change (ΔS_H), latent heat (L), and enthalpy change (ΔE_H) at the DyCo₂ first-order transition obtained from DSC on heating at constant fields.

H (T)	ΔS_H (J kg ⁻¹ K ⁻¹)	$L = \Delta E_H$ (J kg ⁻¹ × 10 ³)
0	8.5	1.2
0.3	8.1	1.1
0.6	6.5	0.9
0.9	6.3	0.9
1.2	5.0	0.7
1.5	4.0	0.6

the field is increased or the temperature raised. The temperature (field) difference between the peaks remains constant as the field (temperature) is increased, so that the peaks coalesce in an unresolved feature as their width increases. At 5 T (90 K) only one wide peak can be observed.

The origin of these two peaks in HoCo₂ as well as the cited minor feature located at a higher temperature in ErCo₂ may be due to sample inhomogeneities. As stated in Sec. II, x-ray diffractograms and energy dispersive spectroscopy assure single phase samples but are compatible with small off-stoichiometry deviations in the samples.

Gratz *et al.*⁵² have reported a strong dependence of the critical temperature with the stoichiometry in the metamagnetic compound ErCo₃. While the stoichiometric sample has an ordering temperature of 100 K, they report that ErCo_{2.88} orders at 65 K. We propose that the additional peaks in the calorimetric curves for HoCo₂ and ErCo₂ samples are a consequence of the presence of a main RCo₂ phase, ordering at T_c , together with a slightly off-stoichiometric phase, ordering at a somewhat different temperature. In fact, the critical temperatures found in the literature vary mostly between 32 K and 34 K for ErCo₂ (Refs. 16–18, 20, 21, 32–39, and 41–43) and 75 K and 78 K for HoCo₂ (Refs. 16, 20, 21, 44, and 41–45). However values from 30 K (Ref. 46) to 36 K (Refs. 4, 15, and 40) and 74 K (Refs. 38 and 39) to 80–95 K (Refs. 4, 18, 40, and 46) can be also found for these compounds, respectively. This leads to the conclusion that their critical temperatures are very sensitive to small deviations in the stoichiometry.

TABLE II. Entropy change, latent heat, and enthalpy change at the HoCo₂ first-order transition obtained from DSC on heating at constant fields (ΔS_H and $L = \Delta E_H$) and increasing the field at a constant temperatures (ΔS_T , L , and ΔE_T).

Constant field			Constant temperature			
H (T)	ΔS_H (J kg ⁻¹ K ⁻¹)	$L = \Delta E_H$ (J kg ⁻¹ × 10 ³)	T (K)	ΔS_T (J kg ⁻¹ K ⁻¹)	$L = T \cdot \Delta S_T$ (J kg ⁻¹ × 10 ³)	ΔE_T (J kg ⁻¹ × 10 ³)
0	20.0	1.6	80	15.0	1.2	1.3
1	17.6	1.4	82	12.9	1.1	1.2
2	14.9	1.3	84	10.6	0.9	1.0
3	12.3	1.1	86	7.9	0.7	0.8
4	10.5	1.0				
5	8.9	0.8				

D. Entropy change, enthalpy change, and latent heat at DyCo₂, HoCo₂, and ErCo₂ ferrimagnetic transitions

ΔS and the latent heat (L) at the transition for the three compounds is determined by numerical integration of $DSC_T(H)$ and $DSC_H(T)$ signals.^{28,30} ΔS and L values for the temperature-induced transition in DyCo₂ are shown in Table I. Values for both temperature- and field-induced transitions are shown in Tables II and III for HoCo₂ and ErCo₂, respectively. As argued before, only data for heating and increasing the field (at a rate of 0.1 T/min) runs are presented. The values are in general agreement with those previously reported from indirect experimental methods and theoretical models.^{15–20,53,54}

In equilibrium, the enthalpy change of a magnetic system at the first-order transition is

$$\Delta E = \int TdS - \int MdH = L - \int MdH, \quad (1)$$

where the integral is evaluated along the transition region.

In isofield experiments, the second term vanishes and $\Delta E_H = L$. In isothermal ones, L is given by $T_c \Delta S_T$ but in order to obtain the enthalpy change ΔE_T , the second term in Eq. (1) has to be evaluated from the magnetization measurements. The obtained ΔE values are also shown in Tables I–III.

It is worth noting that, along the RCo₂ series, $T\Delta S$ is approximately constant, for fixed H/T values. Consequently, ΔS decreases as T_c increases along the series. The univocal relationship between T_c and the critical field H_c allows to assign a temperature for ΔS obtained from isofield measurements and thus in Fig. 9 we show the maximum ΔS values obtained as a function of T_c from both isofield and isothermal DSC measurements. The dashed line is the hyperbolic branch $T\Delta S = 1350$ J/kg, fitting our whole set of data. The data available in literature are consistent with the trend shown in Fig. 9,^{19,20,55} although the agreement with a constant $T\Delta S$ curve is not so good.

The strong variation of ΔS with T had been attributed to the first-order character of the transitions.^{18–20,55} However, it is interesting to note that the ΔS values given in Refs. 19 and 20 for TbCo₂ (which undergoes a second-order magnetic transition with a huge rhombohedral distortion^{59,60}) falls as

TABLE III. Entropy change, latent heat, and enthalpy change at the ErCo₂ first-order transition obtained from DSC on heating at constant fields (ΔS_H and $L=\Delta E_H$) and increasing the field at a constant temperatures (ΔS_T , L , and ΔE_T).

Constant field			Constant temperature			
H (T)	ΔS_H (J kg ⁻¹ K ⁻¹)	$L=\Delta E_H$ (J kg ⁻¹ × 10 ³)	T (K)	ΔS_T (J kg ⁻¹ K ⁻¹)	$L=T \cdot \Delta S_T$ (J kg ⁻¹ × 10 ³)	ΔE_T (J kg ⁻¹ × 10 ³)
0	43.3	1.5	34	36.2	1.2	1.3
1	41.2	1.5	36	34.3	1.2	1.2
2	39.3	1.5	38	31.6	1.2	1.5
3	37.3	1.4				
4	33.0	1.4				
5	29.1	1.3				

well into the same constant- $T\Delta S$ curve (see Fig. 9).

$T\Delta S$ equals L in field-induced transitions and gives a good estimation of the latter in temperature-induced ones. L reflects the energy difference between the high- and low-temperature phases and our results indicate that this energy difference is rather independent of temperature in RCo₂. In principle, the magnetic contribution should show the opposite behavior, as the total magnetic entropy available [$\ln(2J+1)$] is very similar for the three compounds but the critical temperatures (and thus, the exchange energies) vary from about 30 to 150 K. Therefore, the $T\Delta S$ product suggests that the free energy change at the transition is highly dominated by the structural effects, both in first- and second-order RCo₂ ordering transitions.

In contrast, in a first-order transition ruled by the magnetic contribution, one would expect that the magnitude

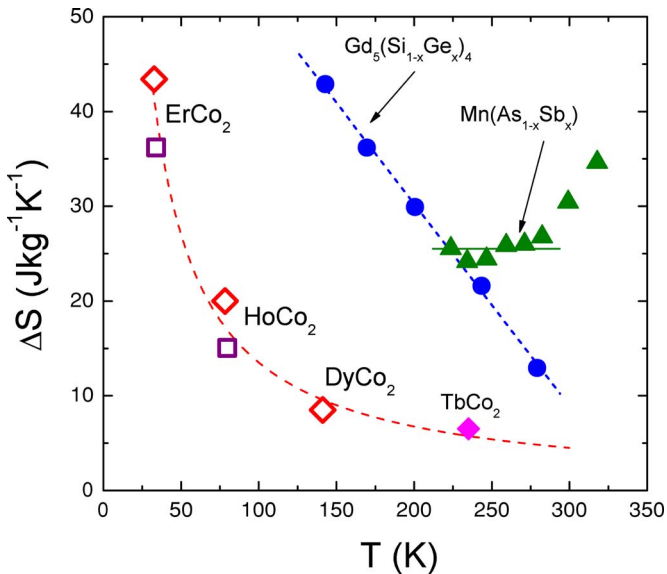


FIG. 9. (Color online) ΔS values as a function of critical temperature at the magnetostructural transitions of some magnetocaloric compounds. Open diamonds and squares are ΔS values for ErCo₂, HoCo₂, and DyCo₂ from isofield and isothermal DSC measurements, respectively. Full circles are ΔS for Gd₅(Si_xGe_{1-x})₄ (Refs. 29, 56, and 57), full triangles for MnAs_{1-x}Sb_x (Refs. 55 and 58), and full diamond for TbCo₂ (Refs. 19 and 20).

which remains constant as a function of temperature should be the entropy [dominated by the $\ln(2J+1)$ term] instead of the latent heat. This is indeed the case for a certain range of compositions ($x=0.1-0.3$) and temperatures (222–300 K) in the MnAs_{1-x}Sb_x first-order transitions,^{55,58} as shown in Fig. 9. This fact is very important for technological reasons, as that family would allow to prepare a useful composite for magnetic cooling below room temperature.⁵⁸ An intermediate case is Gd₅(Si_xGe_{1-x})₄, for which selected data^{29,56,57} are also shown in Fig. 9.

The results on Gd₅(Si_xGe_{1-x})₄ allowed to some of us to point out the scaling of ΔS with T_c in this family for a wide range of temperatures and compositions,⁵⁶ reflecting a balance between structural and magnetic effects at the first-order transition.

In order to study the differences in the entropy change obtained from isofield and isothermal DSC experiments, we have also determined ΔS at the transition from isofield and isothermal magnetization curves applying the Clausius-Clapeyron equation

$$\Delta S = -\Delta M \frac{dH_c}{dT_c} \quad (2)$$

or from isothermal magnetization curves applying the Maxwell relations within the transition region^{61,62}

$$\Delta S = \int_{H_a}^{H_b} \left(\frac{\partial M}{\partial T} \right)_H dH \quad (3)$$

(where the transition takes place between H_a and H_b).

When applying the Clausius-Clapeyron equation, the magnetization jump (ΔM) at the transition has to be evaluated. Since real transitions occur within a range of temperature and field, contributions coming from other phenomena occurring in the same region should be separated. In particular, for the $M(H)$ curves, the magnetization process due to the increase of the applied magnetic field has to be subtracted. For this reason, the $M(H)$ curve is linearly extrapolated in the vicinity of the transition region for the paramagnetic phase as well as for the ferrimagnetic phase (see Fig. 10). The points where the curve diverges from the two straight lines define the transition limits. ΔM is then evalu-

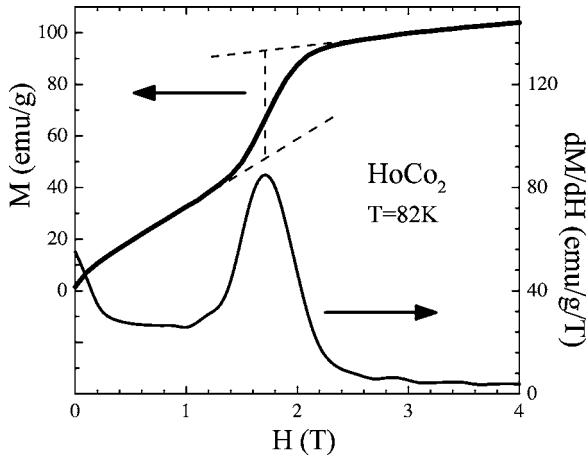


FIG. 10. $M(H)$ and its derivative in HoCo_2 at 82 K.

ated as the difference between the lines at the critical field, which is defined for each isothermal $M(H)$ curve as the field corresponding to the inflection point within the transition region (see Fig. 10). For $M(T)$ curves, the same procedure can be applied to determine ΔM and the transition limits. In this case, the two lines are parallel (see Fig. 11).

Figure 12 shows the values of ΔS obtained from both calorimetric data and magnetization curves as a function of the temperature for HoCo_2 . We compare ΔS obtained from magnetization and calorimetric data and for both temperature and field induced transitions. It is worth stressing the agreement between ΔS obtained from $\text{DSC}_H(T)$ and from $M(T)$ using the Clausius-Clapeyron equation [$\text{C-C}_{M(T)}$ in the figures]. Besides, we also point out the agreement between ΔS obtained from $\text{DSC}_T(H)$ and from $M(H)$ using the Clausius-Clapeyron equation [$\text{C-C}_{M(H)}$] and the Maxwell relation [Eq. (3)]. Provided that the transition is induced by the same driving physical parameter, either T or H, the agreement between the calorimetric and magnetic data, although very satisfactory, was indeed expected.

In contrast, ΔS values obtained from isofield measurements are 20% larger than those obtained from isothermal measurements for the lower temperatures and fields and up

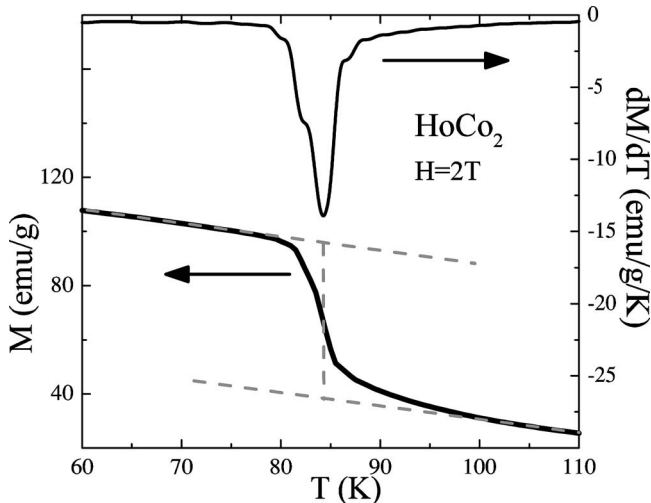


FIG. 11. $M(T)$ and its derivative in HoCo_2 at 2 T.

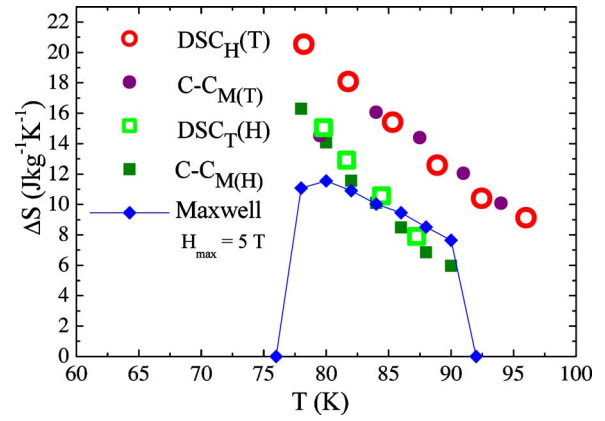


FIG. 12. (Color online) Entropy change for HoCo_2 calculated (i) from DSC measurements sweeping the temperature (open circles) and sweeping the field (open squares), (ii) from $M(T)$ and $M(H)$ using the Clausius-Clapeyron equation (full circles and full squares, respectively), and (iii) from $M(H)$ using the Maxwell relation being 5 T the maximum applied magnetic field (full diamonds; continuous line is drawn as a guide to the eye).

to 50% larger for the higher temperatures and fields.

For ErCo_2 , ΔS values have been obtained from calorimetric and magnetization data as described in Ref. 64. Values are shown in Fig. 13 as a function of the temperature. As for the HoCo_2 compound, the agreement in ErCo_2 among ΔS values obtained from isofield measurements on one hand and among the isothermal results on the other is remarkable. Furthermore, isofield values are also up to 25% higher than the isothermal ones.

This data analysis is not applicable to the DyCo_2 sample due to the extreme broadness of the transition. First, in the calorimetric curves at constant temperature, it is not possible to estimate a baseline for the lower fields and hence the integration of the signal is not reliable. Second, and as stated in Sec. II, the shape of $M(H)$ curves do not allow to estimate

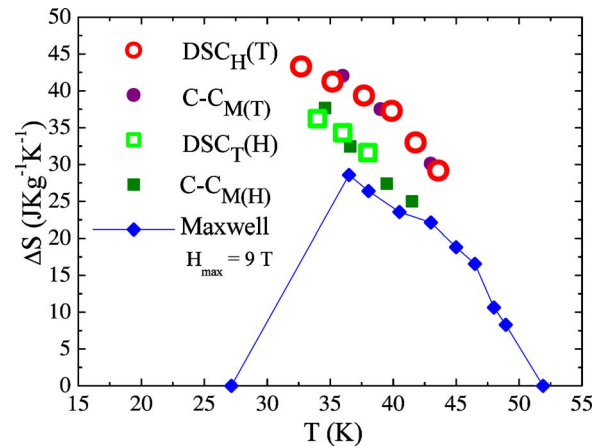


FIG. 13. (Color online) Entropy change for ErCo_2 calculated (i) from DSC measurements sweeping the temperature (open circles) and sweeping the field (open squares), (ii) from $M(T)$ and $M(H)$ using the Clausius-Clapeyron equation (full circles and full squares, respectively), and (iii) from $M(H)$ using the Maxwell relation being 9 T the maximum applied magnetic field (full diamonds, continuous line is drawn as a guide to the eye).

the magnetization jump and thus ΔS at transition. Consequently, we could not obtain isothermal ΔS values in DyCo_2 to compare them with the corresponding isofield values.

At least three phenomena may lead to the mentioned difference in ΔS obtained from isofield and isothermal measurements, all of them being a consequence of the nonideality of the first-order transition. In the isothermal process, the applied magnetic field is increased throughout the transition region and, hence, magnetic work is done to the system. This fact produces an additional negative contribution to the entropy change which can be estimated as

$$w = \frac{1}{T} \int_{H_a}^{H_b} M dH, \quad (4)$$

where the integral extends only over the transition region.⁶³ In the case of HoCo_2 , this term accounts for 20–30% of the difference between the values of ΔS obtained from isofield and isothermal processes, while for ErCo_2 , this term is strongly dependent on the temperature. In a range of 5 K, the term $(1/T) \int M dH$ varies from 10% to 100% of the difference between ΔS obtained from isofield and isothermal measurements. Moreover, the broadness of the transition also implies that the initial and final states involved in the two different kinds of experiments are not equivalent. Hence we want to stress that care should be taken when comparing ΔS values obtained from experiments in which the driving physical parameters are different.

Finally, the presence of hysteresis, as evidenced in Figs. 5 and 6, reveals that the samples did not reach full thermodynamical equilibrium during the experiments, in which the transitions spanned over a time window of the order of 10^2 – 10^3 s. The Maxwell relations and the Clausius-Clapeyron equation are valid only in equilibrium, but the agreement between ΔS obtained from the analysis of magnetization data and those obtained directly from DSC indicates that this is not at the origin of the differences observed (see Figs. 12 and 13). Conversely, the lack of thermodynamical equilibrium may lead to dissipation and might account, at least partially, for the differences in ΔS between field and temperature driven transitions.

IV. CONCLUSIONS

To conclude, we review the most relevant results obtained in this work:

(i) In contrast with recent experiments,²³ the results from our DSC measurements under applied field in PrCo_2 and NdCo_2 reveal unambiguously the second-order nature of their ferromagnetic transitions.

(ii) The calorimetric curves for ErCo_2 and HoCo_2 ob-

tained by sweeping the temperature at different fields and sweeping the field at different temperatures show the expected features for a first-order transition: sharp peaks, temperature and field hysteresis, and dependence of the critical temperature with the applied field. DyCo_2 shows the typical dependence of the critical temperature with the applied field for a first-order transition. However the corresponding calorimetric curves show rather broad peaks and no thermal or field hysteresis, evidencing the weak first-order character of the transition.

(iii) Three main peaks are observed in ErCo_2 calorimetric curves as well as in the derivative of $M(H)$, which we relate with the anisotropy of the coexistence curve H_c - T_c found in the ErCo_2 single crystal.⁵⁰

(iv) The latent heats, entropy changes, and critical temperatures obtained from our DSC measurements suggest that the latent heats in RCO_2 are governed by the structural changes at the transition.

(v) We have determined ΔS from DSC and magnetization data in ErCo_2 and HoCo_2 . This analysis demonstrates that isofield and isothermal processes yield different ΔS values at the magnetostructural transition. The work that the magnetic field does over the system⁶³ in the isothermal process accounts for a fraction of the difference. However, the broadness of their transitions also implies that the initial and final states involved in the two kinds of processes are not the same and therefore ΔS at the isothermal and isofield transitions may be different, depending on the particular shape of the $M(H, T)$ surface. This fact not only explains discrepancies that appear in the literature concerning the RCO_2 series^{15–20} but also other systems, as the giant magnetocaloric $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$ alloys.⁶³ The magnitude of the discrepancies (up to 50% in some cases) imply that in order to appropriately evaluate ΔS in materials of potential use in cooling devices, the path followed to induce first-order magnetostructural transitions should be carefully taken into account.

ACKNOWLEDGMENTS

This work has been partially funded by the Fundación Areces, the Spanish CICYT research Projects Nos. MAT2002-04178-C04-03, MAT2005-002454, and MAT2003-01124, the FEDER program, the Aragonese CAMRADS research group, and the Catalan DURSI research Project No. 2001SGR00066. We thank N. Plugaru and M. J. Pastor for sample preparation, Ll. Mañosa, A. Planes, and L. Morellón for fruitful discussions, J. Rodríguez and J. Sánchez-Marcos for their magnetization facilities at the Universidad de Cantabria, and J. Bartolomé for a critical reading of the manuscript. J.H. acknowledges MEC for the Ph.D. grant.

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