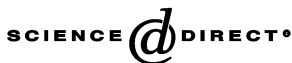




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Entropy change at the magnetostructural transition in RCo_2 (R = Dy, Ho, Er)

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Abstract

Differential scanning calorimetry under applied magnetic field has been used to characterize the magnetocaloric effect in ErCo_2 , HoCo_2 , and DyCo_2 . The entropy change ΔS at the first-order magnetostructural transition present in these materials has been studied by inducing the transition; sweeping the temperature at a constant field and sweeping the field at a constant temperature. The corresponding values of ΔS differ significantly due to the broadness of the transition, i.e. the initial and final states involved when the transition is field or temperature induced are different. In the field-induced case, the additional work done by the magnetic field extending through the region in which the transition spread accounts roughly for the observed difference.

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Magnetic compounds displaying first-order magnetic phase transitions are of great interest as potential magnetocaloric materials, since magnetization changes abruptly in a narrow temperature range. In particular, the RCo_2 Laves phases with

R = Dy, Ho and Er show a first-order magnetostructural transition between para- and ferrimagnetic states. The high values of the magnetic moment for Dy, Ho and Er give rise to a remarkable entropy change (ΔS) at the transition. The magnetic moment of Co in RCo_2 is induced by either the applied field or the rare-earth molecular field [1], yielding a negligible contribution to ΔS [2]. The large ΔS at the transition has motivated various studies on the magnetocaloric

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effect (MCE) in these compounds [3,4]. In fact, one open question is to elucidate the effect on ΔS of the broadness of the transition when it is field- or thermally-induced. This is relevant when comparing MCEs obtained from the two usual experimental procedures: from calorimetric data at a constant field or from isothermal magnetization curves. The aim of this work is to study these issues in DyCo_2 , HoCo_2 and ErCo_2 and to justify the differences observed between published data for ErCo_2 from different authors [5,6].

Heat capacity measurements are often used to obtain the relevant magnitudes of MCE. However, it is well known that severe intrinsic errors may affect the evaluation of MCE from heat capacity in the vicinity of a first-order phase transition due to the release/absorption of latent heat [7]. By contrast, differential scanning calorimetry (DSC) is one of the most suitable methods to study first-order phase transitions. In DSC, the heat flow between the sample and a thermal block is measured while the temperature is recorded. Consequently, the main contribution to the calorimetric signal is the heat flow absorbed or released by the sample during the first-order transition. Then, latent heat and ΔS can be accurately determined from a proper integration of the calorimetric signal.

We have studied the magnetostructural transition in polycrystalline RCO_2 samples ($R = \text{Dy}$, Ho , and Er), carrying out DSC measurements by sweeping the temperature at a constant field [$\text{DSC}_H(T)$] or by sweeping the field at a constant temperature [$\text{DSC}_T(H)$]. The maximum available magnetic field was 5 T. A detailed description of the experimental set up can be found in Ref. [8].

Samples were prepared by melting the pure elements in an induction furnace under Ar atmosphere and were further annealed at 850°C for a week. X-ray diffraction analysis showed that samples were single phase. Magnetization measurements $M(T, H)$ have been carried out with extraction and SQUID magnetometers. At zero field, the transition temperature to the ferrimagnetic state for DyCo_2 , HoCo_2 , and ErCo_2 is 142, 78 and 34 K, respectively. The magnetic characterization is fully consistent with that previously reported [1].

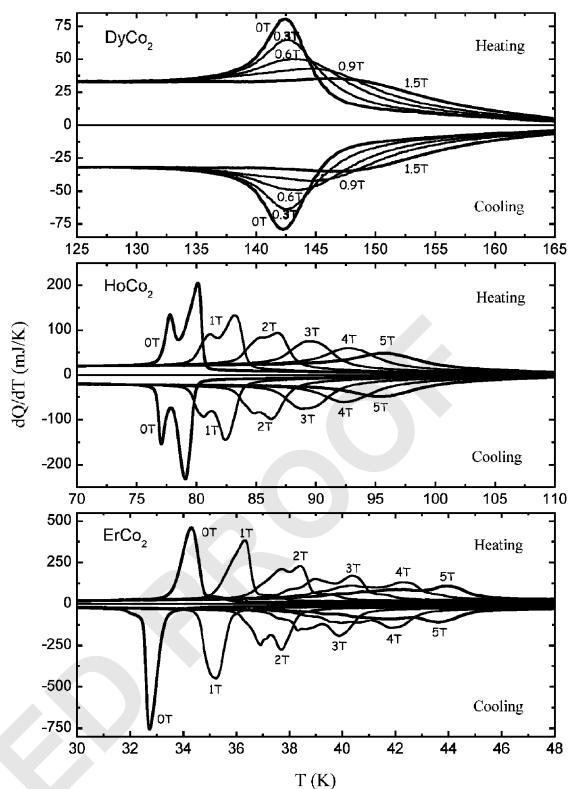


Fig. 1. Heating and cooling runs of DSC measurements at constant applied magnetic fields for DyCo_2 , HoCo_2 , and ErCo_2 .

In Fig. 1, the calorimetric curves for ErCo_2 and HoCo_2 show the expected features for a first-order transition: sharp peaks, thermal hysteresis, and a strong variation of the critical temperature, T_c , with the applied field. At zero field, the calorimetric curve for ErCo_2 displays a single peak which splits in three overlapping peaks under applied field. In this compound, for a fixed magnetic field, T_c depends on the relative orientation of the field with respect to the three crystallographic directions [9]. Therefore, in a polycrystalline sample, three different ordering temperatures are observed together with a strong broadening of the transition region with the applied field. The splitting is not observed in HoCo_2 , in accordance with the reported lack of dependence in T_c with the orientation of the applied field [1]. In this case, the double peak structure, which is already present at zero field, is

essentially field independent and it may be attributed to sample inhomogeneities [10].

By contrast, calorimetric curves for DyCo_2 show a broad peak which tends to be even broader as the field increases, becoming almost inappreciable at 5 T. Besides, T_c exhibits a strong field dependence, although no thermal hysteresis is observed in contrast with previous DSC results at zero field [11]. These effects may originate from the small size of the discontinuity of the free energy derivatives at the DyCo_2 transition suggested by numerous experimental results [1,12].

ΔS at the transition for the three compounds is determined by numerical integration of $\text{DSC}_T(H)$ and $\text{DSC}_H(T)$ signals. The ΔS values obtained are shown in Table 1, and are in agreement with those previously reported from indirect experimental methods and theoretical models [13,14].

Fig. 2 shows the $M(H, T)$ surface for ErCo_2 obtained from isofield and isothermal magnetization curves. From these data, ΔS can be also determined by applying the Maxwell relations or the Clausius–Clapeyron equation (C–C) to the analysis of $M(H)$ isotherms [15]. However, the determination of the transition region in which these equations should be applied is difficult and, indeed, it is easy to overestimate the limits of the transition region from the $M(H, T)$ surface. Therefore, the range of the transition region have been determined from the DSC curves and it has been applied to the $M(H)$ curves. Bold lines in Fig. 2 show examples of the determination of the transition regions in an isothermal and an isofield curve.

In Fig. 3, the values of ΔS obtained from both calorimetric data and $M(H)$ isotherms are shown as a function of the temperature for ErCo_2 , taking advantage of the univocal relationship between T_c and the critical field H_c . This critical field is defined for each isothermal $M(H)$ curve as the field corresponding to the inflection point within the transition region. Fig. 3 shows that ΔS from $\text{DSC}_T(H)$ is about 15% lower than ΔS from $\text{DSC}_H(T)$. This difference was already present between ΔS values obtained from the calorimetric data at a constant field reported by Wada et al. [5]

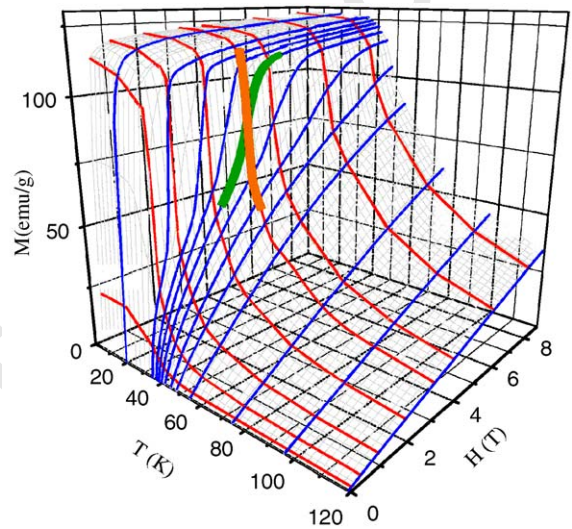


Fig. 2. (Color online) Magnetization of ErCo_2 as a function of T and H . For the sake of clarity, only some representative curves are shown. Bold lines indicate the transition region corresponding to an isothermal and an isofield curve.

Table 1

ΔS at the first-order transition obtained from DSC on heating at a constant field (ΔS_H) for DyCo_2 , HoCo_2 and ErCo_2 and increasing the field at a constant temperature (ΔS_T) for ErCo_2

DyCo_2		HoCo_2		ErCo_2			
$H(T)$	ΔS_H ($\text{Jkg}^{-1}\text{K}^{-1}$)	$H(T)$	ΔS_H ($\text{Jkg}^{-1}\text{K}^{-1}$)	$H(T)$	ΔS_H ($\text{Jkg}^{-1}\text{K}^{-1}$)	$T(\text{K})$	ΔS_T ($\text{Jkg}^{-1}\text{K}^{-1}$)
0	8.5	0	20.0	0	43.3	34	36.2
0.3	8.1	1	17.6	1	41.2	36	34.3
0.6	6.5	2	14.9	2	39.3	38	31.6
0.9	6.3	3	12.3	3	37.3		
1.2	5.0	4	10.5	4	33.0		
1.5	4.0	5	8.9	5	29.1		

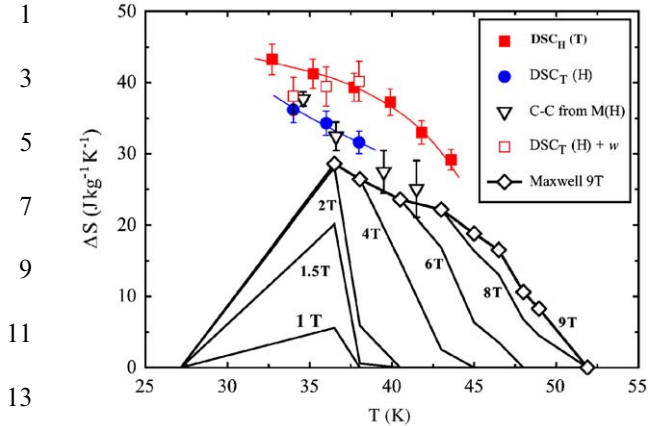


Fig. 3. (Color online) ΔS for ErCo_2 obtained by different methods as indicated in the legend. The continuous lines correspond to ΔS from Maxwell relations evaluated up to a maximum field, which is indicated beside each curve.

and ΔS values obtained from the isothermal magnetization curves reported by Duc and Kim Anh [6]. The disagreement is a consequence of the non-ideality of the first-order transition and the anisotropy of the $T_c(H_c)$ curve, which give rise to an intrinsically wide transition region (see bold lines in Fig. 2). Therefore, while measuring $\text{DSC}_T(H)$, the applied magnetic field is actually being increased throughout the transition region. As a result, a magnetic work is done over the system producing an additional contribution to the entropy change, which can be estimated as $w = 1/T \int M dH$, where the integral extends only over the transition region [16].

w has been calculated from $M(H)$ curves shown in Fig. 2 for the three temperatures at which $\text{DSC}_T(H)$ was measured. These values have been added to ΔS as obtained from $\text{DSC}_T(H)$, and the results are also plotted in Fig. 3, showing a very good agreement with ΔS as obtained from $\text{DSC}_H(T)$ curves. Obviously, w is non-zero when the transition is field-induced and extends over a certain field range [16]. Indeed, actual field-induced transitions spread over a finite region, w always being non-zero. In the case of polycrystalline ErCo_2 , the field range is very broad due to the anisotropy of the coexistence curve.

It is worth stressing that ΔS obtained from $\text{DSC}_T(H)$ is in excellent agreement with ΔS

estimated from $M(H)$ data, either calculated from the Clausius–Clapeyron equation or from the Maxwell relations, provided that the maximum field is high enough to complete the transition and the Maxwell relation is evaluated only within the transition region. This agreement is expected since both sets of data (calorimetric and magnetic) have been measured following the same procedure; in which the field is increased at a constant temperature. In contrast, ΔS from $\text{DSC}_H(T)$ data is significantly larger since in this case the temperature is swept at a constant H and consequently other initial and final states in the phase diagram are involved, as can be clearly seen in Fig. 2 (bold lines).

To conclude, we have characterized MCE in RCO_2 by determining ΔS from DSC data sweeping the magnetic field and the temperature, and compared this with ΔS from magnetization measurements. From this analysis, we have demonstrated that in compounds with an extended critical region on the phase diagram [$M(T, H)$ surface], e.g. ErCo_2 , isofield or isothermal processes yield different ΔS values at the magnetos-structural transition. Therefore, depending on the details of the phase diagram, care should be taken when comparing MCE from different experimental procedures because different initial and final states are involved in the two processes.

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