Entropy change at the magnetostructural transition in $\text{RCO}_2$ ($R = \text{Dy, Ho, Er}$)

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Received 7 April 2005; received in revised form 24 June 2005

Abstract

Differential scanning calorimetry under applied magnetic field has been used to characterize the magnetocaloric effect in $\text{ErCO}_2$, $\text{HoCO}_2$, and $\text{DyCO}_2$. The entropy change $\Delta S$ 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 $\Delta S$ 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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PACS: 75.30.Et; 75.40Cx; 65.40.+g

Keywords: ; ; ;

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 $\text{RCO}_2$ Laves phases with $R = \text{Dy, Ho and Er}$ 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 ($\Delta S$) at the transition. The magnetic moment of Co in $\text{RCO}_2$ is induced by either the applied field or the rare-earth molecular field [1], yielding a negligible contribution to $\Delta S$ [2]. The large $\Delta S$ 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 $\Delta S$ 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 $\Delta S$ can be accurately determined from a proper integration of the calorimetric signal.

We have studied the magnetostructural transition in polycrystalline RCo$_2$ samples (R = Dy, Ho, and Er), carrying out DSC measurements by sweeping the temperature at a constant field [DSC$_H(T)$] or by sweeping the field at a constant temperature [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].

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 DyCo₂ 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].

In Fig. 3, the values of $\Delta S$ obtained from both calorimetric data and $M(H)$ isotherms are shown as a function of the temperature for ErCo₂, 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 $\Delta S$ from DSC$_{T}(H)$ is about 15% lower than $\Delta S$ from DSC$_{H}(T)$. This difference was already present between $\Delta S$ values obtained from the calorimetric data at a constant field reported by Wada et al. [5].

$\Delta S$ at the transition for the three compounds is determined by numerical integration of DSC$_{T}(H)$ and DSC$_{H}(T)$ signals. The $\Delta S$ 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 ErCo₂ obtained from isofield and isothermal magnetization curves. From these data, $\Delta S$ 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.

<table>
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<th>$H(T)$</th>
<th>$\Delta S_H$ (J kg$^{-1}$K$^{-1}$)</th>
<th>$H(T)$</th>
<th>$\Delta S_H$ (J kg$^{-1}$K$^{-1}$)</th>
<th>$H(T)$</th>
<th>$\Delta S_H$ (J kg$^{-1}$K$^{-1}$)</th>
<th>$T$(K)</th>
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Table 1
$\Delta S$ at the first-order transition obtained from DSC on heating at a constant field ($\Delta S_H$) for DyCo₂, HoCo₂ and ErCo₂ and increasing the field at a constant temperature ($\Delta S_T$) for ErCo₂.
and $\Delta S$ 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 $\Delta S$ obtained from $DSC_T(H)$, 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 $DSC_T(H)$ was measured. These values have been added to $\Delta S$ as obtained from $DSC_T(H)$, and the results are also plotted in Fig. 3, showing a very good agreement with $\Delta S$ as obtained from $DSC_H(T)$ 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 $\Delta S$ obtained from $DSC_T(H)$ is in excellent agreement with $\Delta S$ 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, $\Delta S$ from $DSC_H(T)$ 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 $\Delta S$ from $DSC$ data sweeping the magnetic field and the temperature, and compared this with $\Delta S$ 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 $\Delta S$ values at the magnetostuctural 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.

This work has been partially funded by the Fundación Areces, the Spanish CICYT research projects MAT2002-04178-C04-03 and MAT2003-01124, the FEDER program and the Catalan DURSI research project 2001SGR00066. We thank Dr. N. Plugaru and M.J. Pastor for sample preparation, Dr. Ll. Mañosa for fruitful discussion and Dr. J. Rodríguez and J. Sánchez for their magnetization facilities at the Universidad de Cantabria. J.H. and F.C. acknowledge MEC and Catalan DURSI for Ph.D Grants.

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