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Metamagnetic transition and magnetocaloric effect in ErCo_2

A Giguere^{†§}, M Foldeaki^{†||}, W Schnelle^{‡¶} and E Gmelin[‡]

[†] Institute de Recherche sur l'Hydrogene, CP 500 Trois-Rivieres, Quebec, Canada G9A-5H7

[‡] Max-Planck-Institut für Festkörperforschung, Heisenbergstraße 1, 70569 Stuttgart, Germany

E-mail: alexandre.giguere@uqtr.quebec.ca, maria.foldeaki@attcanada.net,
schnelle@cpfs.mpg.de and gmelin@servix.mpi-stuttgart.mpg.de

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Abstract. The magnetization $M_H(T)$ and the specific heat capacity $c_{P,H}(T)$ of the ErCo_2 intermetallic compound were measured in the temperature range 5–100 K and in 0, 7 or 14 T applied field, respectively. A clear first-order phase transition is found at the magnetic ordering of the Er sublattice. While for order–disorder transitions in simple ferromagnets there is a good agreement between magnetocaloric performance predicted on the basis of magnetization measurements compared to calorimetric measurements, it is necessary to investigate whether the agreement is still present for materials with more complex transitions (e.g. order–order, metamagnetic, first order etc). From the magnetization data the magnetic entropy change at the transition was calculated using the Maxwell relations. From the $c_{P,H}(T)$ measurements both the magnetic entropy change and the adiabatic temperature change were calculated and compared to values obtained from $M_H(T)$ and to the values calculated by the usual approximative expressions. The agreement is less good than in the case of second-order phase transitions. The discrepancy is interpreted in terms of the theory of first-order/metamagnetic transitions showing that the boundary conditions used in the derivation of the approximative formulae for simple ferromagnetic materials are not appropriate for more complex transitions as in ErCo_2 .

1. Introduction

Beyond its potential interest as a magnetic regenerator [1] or refrigerator [2] material, ErCo_2 and the family of the RCO_2 -type cubic Laves-phase compounds (R = rare earth) offer an opportunity to study complex magnetic interactions, like the metamagnetic transition of the itinerant d-electron subsystem as a function of both internal and external magnetic fields [3]. In these intermetallic compounds, the presence of magnetic order in the R sublattice can induce a moment on the Co site, which in turn may drive the transition into first order for some compositions [4].

In RCO_2 intermetallics, the Co 3d band is ‘nearly magnetic’. A metamagnetic state due to splitting the majority and minority 3d sub-bands of Co may be achieved by exposing YCo_2 or LuCo_2 to external magnetic fields at approximately 70 T [5, 6]. Similarly, 4f moments, which order ferromagnetically at T_C , yield a strong exchange field acting on the Co 3d states. When this field is sufficient to split the 3d majority and minority sub-bands, the spin fluctuations at the Co sites are quenched, and the 3d magnetic band metamagnetic state with moments on Co sites is induced by a first-order transition for $\text{R} = \text{Dy}, \text{Ho}$ and Er . This process occurs

§ Present address: Laboratoire Louis Néel–CNRS, 25 Avenue des Martyrs, BP 156, 38042 Grenoble Cedex 9, France.

|| Present address: POB 1841 Station ‘B’, Montreal, Quebec H3B 3L4, Canada.

¶ Present address: Max-Planck-Institut für Chemische Physik fester Stoffe, Pirnaer Landstraße 176, D-01257 Dresden, Germany.

at T_0 ($< T_C$) in zero magnetic field or at higher temperatures if the exchange field is assisted by a sufficiently large external magnetic field [5]. The metamagnetic transition results in a decrease of the magnetic entropy [3]. Mössbauer effect measurements found a ferromagnetic ordering temperature $T_C = 35.7$ K [7] via extrapolating the linear decrease of long range order of Er moments in the co-operative phase from the spectra observed between 30 K and 35 K. The temperature $T_C = 35.7$ K indicates the beginning of the completely disordered phase, i.e. above which temperature the magnetization begins to drop rapidly. Neutron diffraction data yield $T_C = 39$ K and magnetic moments of $8.9 \pm 0.2 \mu_B$ for Er and $-1.0 \pm 0.2 \mu_B$ for Co [8] in agreement with the saturation moment of $7.0 \mu_B$ per ErCo_2 and with the free ion value of $9 \mu_B$ for Er found by the Mössbauer effect.

A double transition was observed in $\text{Er}_{0.6}\text{Y}_{0.4}\text{Co}_2$ [9]. A second-order phase transition takes place at $T_C^R = 14.5$ K to magnetic ordering within the R sublattice followed by a first-order phase transition at $T_C^{\text{Co}} = 11$ K due to metamagnetic behaviour of the itinerant d-electron subsystem. Similar first-order phase transitions are observed in DyCo_2 ($T_0 = 140$ K), HoCo_2 ($T_0 = 75$ K) and ErCo_2 ($T_0 = 33$ K) accompanied by the appearance of a Co moment [10]. These RCO_2 compounds are ferrimagnetic, i.e. the direction of the Co moment is opposite to that of the R moments. The difference between the observed first-order transition temperature and the Er ordering temperature obtained by microscopic methods [7, 8] proves the theoretically predicted double transition in ErCo_2 [11].

A thermodynamic analysis is hindered by the fact that for the first-order transition it is difficult to separate the magnetic part of the entropy change ΔS [12]. The magnetic entropy change at the transition ($\Delta S_{\text{FI-F}}$ —where FI indicates the ferrimagnetic and F the ferromagnetic phase) includes not only the change in spin entropy ΔS_{mo} but also the electronic entropy change ΔS_e and the lattice entropy change ΔS_l at T_0 . The F-P (P = paramagnetic phase) transition might not be described by a localized moment model either. This way:

$$\Delta S_{\text{FI-F}} = \Delta S_l + \Delta S_e + \Delta S_{\text{mo}} \quad (1)$$

where ΔS_{mo} represents the entropy change due to a difference in the degree of magnetic order between the F and AF states. This term should originate in a difference in the magnetic order (mo) parameter between the F and AF states at T_0 , if it exists. Although we have no reliable theory to calculate ΔS_{mo} for a transition involving itinerant electrons, the relative sublattice magnetization can be considered as an important factor to determine ΔS_{mo} from an analogy of a localized model.

The present study is aimed at the more detailed description of the temperature and field driven phase transitions in ErCo_2 . For the first time specific heat data measured in high magnetic fields for this material are presented. The data offer the opportunity to investigate the range of validity of the approximative numerical methods for the calculation of magnetocaloric properties.

2. Experimental methods

Stoichiometric ErCo_2 samples were processed in an arc furnace under argon atmosphere. Figure 1 shows the x-ray diffraction patterns of the two samples prepared. Sample A was small (~ 8 g) and cooled from the melting point to room temperature in about 2 minutes. The x-ray diffraction pattern (figure 1(a)) proves that it is pure, single phase, stoichiometric ErCo_2 . Sample B was larger (~ 25 g) and needed about 5 minutes to cool. X-ray diffraction reveals the presence of a minor additional phase (see figure 1(b)). Magnetic and specific heat measurements were carried out on sample A. Magnetocaloric adiabatic temperature change was measured on sample B in a device developed by Gopal *et al* [13]. Magnetization data were

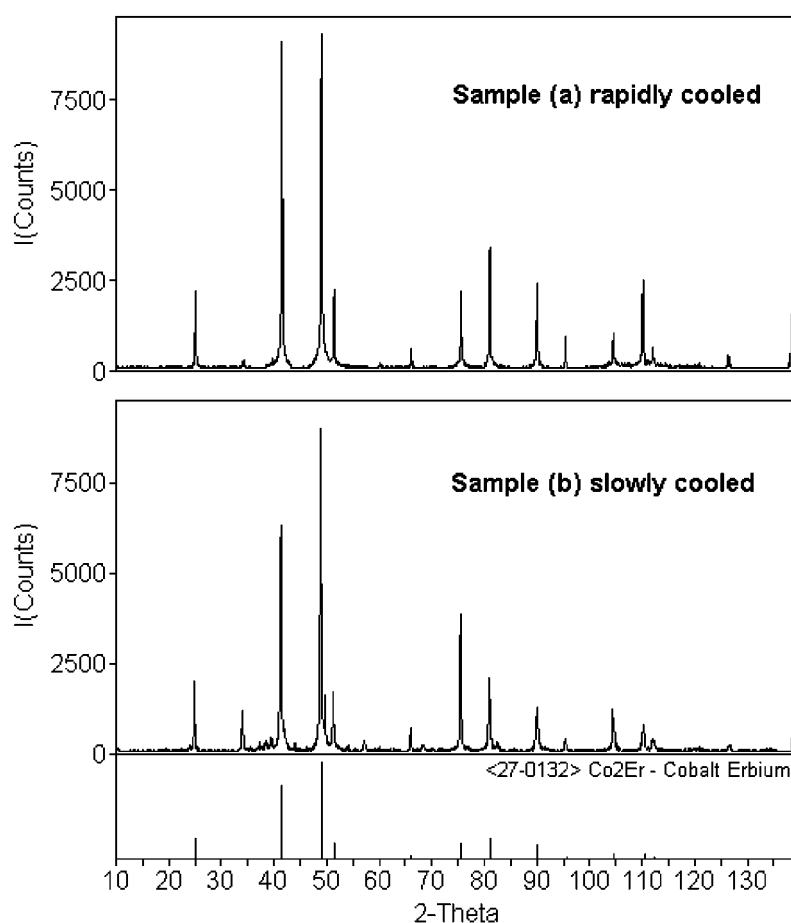


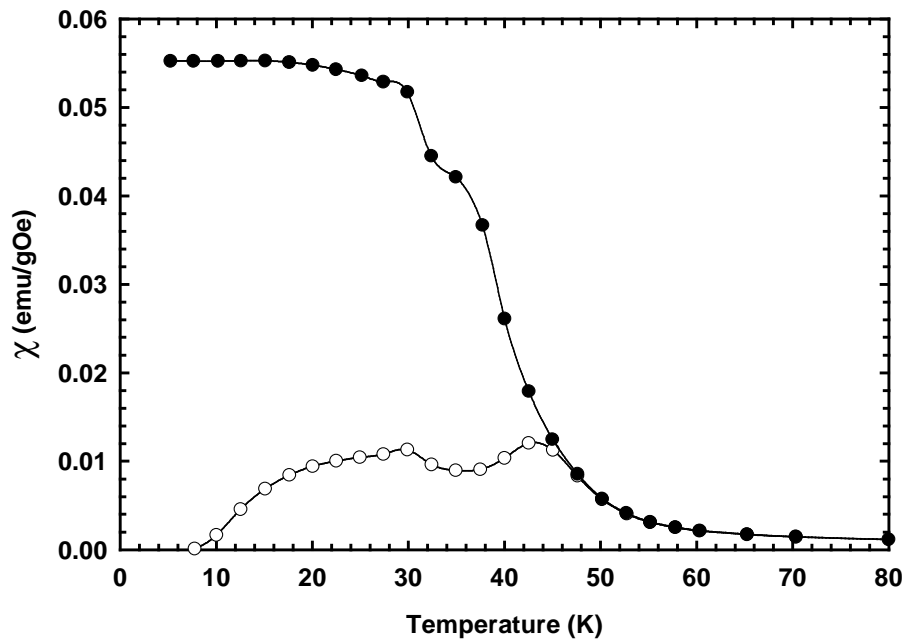
Figure 1. X-ray diffraction pattern of rapidly (a; sample A) or slowly (b; sample B) cooled ErCo_2 .

measured in a commercial SQUID magnetometer. Specific heat measurements were carried out in an improved version of a vacuum calorimeter as described by Gmelin [14].

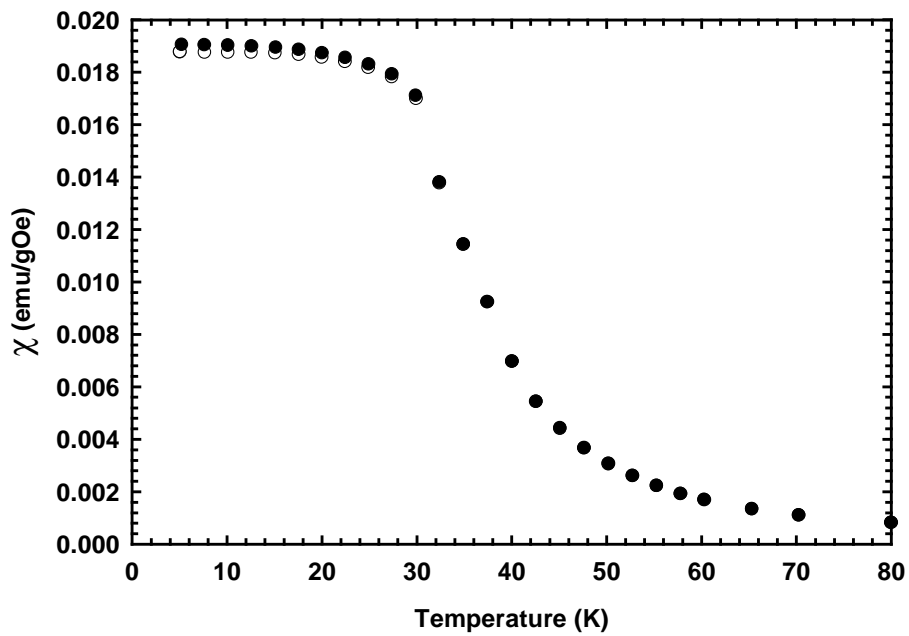
The magnetic entropy change was calculated from magnetization data $M_T(H)$ by the Maxwell relation [15], using approximative numerical integration [16] or as the difference of the entropies calculated from the specific heat $c_{P,H}(T)$ measured with or without applied magnetic field H [15, 17].

3. Results and discussion

Figure 2 displays low and high field susceptibility after zero field cooling (zfc) or field cooling (fc). In low fields, two peaks can be clearly observed after zfc, at the P–F and F–FI transition temperatures. The upper peak appears at temperatures higher than the observed Er ordering temperature, proving the presence of exchange-enhanced paramagnetism [3, 4], intrinsic in ErCo_2 alloys. As the field increases, the upper peak is reduced to an inflexion point and then smeared out, and the lower peak is replaced by a plateau down to the lowest measuring temperature. The fc susceptibility displays only the plateau at all investigated fields. Simultaneously, zfc and fc susceptibilities are different as for a spin-glass. This can be



(a)



(b)

Figure 2. (a) Low (100 Oe) and (b) high (5000 Oe) field susceptibility of ErCo_2 after zfc (○) or fc (●).

qualitatively understood on the basis of Co–Er interaction. The Co moment is induced by the exchange field of the Er, but these induced moments influence the Er exchange thereafter, thus

stabilizing spin directions during cooling via conduction electron polarization. Consequently, the zero-field susceptibility is small at low temperatures. For field cooling, the spins are stabilized along the field directions. The zero-field susceptibility peaks near the first-order transition; consequently, for lower applied fields there are regions with $dM/dT > 0$ near the transition temperature, resulting from the complex nature of the transition.

An alternative explanation of the behaviour can be offered on the basis of magnetic anisotropy, which is high in rare-earth/transition metal based intermetallic compounds. Near the Curie temperature, the magnetic anisotropy approaches zero, having therefore little impact on the low-field magnetic behaviour. As the temperature decreases, the anisotropy increases, and the force provided by low fields is not sufficient to change the direction of magnetic moments, thus the susceptibility remains low—close to zero—after zero field cooling, as the moments' directions are random. Field cooling stabilizes the magnetic moments along the field direction (or along the closest preferred direction) near the Curie temperature, consequently the field cooled susceptibility remains high even at low temperatures. The plateau corresponds to the equilibrium external fields and anisotropy forces.

The high-field/high temperature susceptibility displays simple Curie–Weiss behaviour, giving 33.9 K as Weiss constant and $9.16 \mu_B$ as effective magnetic moment on Er atoms, in good agreement with Mössbauer/neutron diffraction results [7, 8].

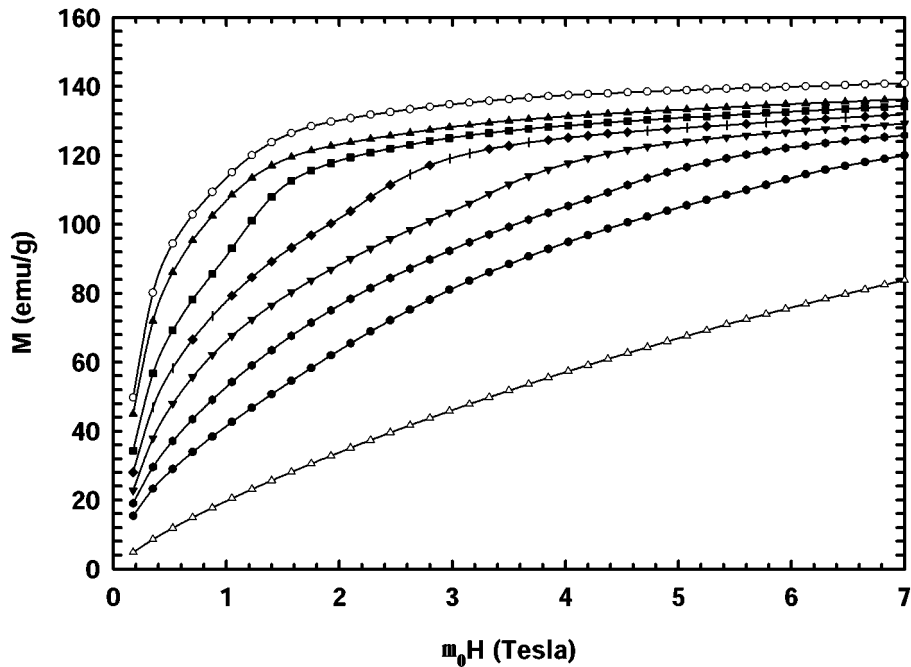


Figure 3. Isothermal magnetization curves at different temperature ranges/phase regions. $T < 33$ K: ferrimagnetism. $33 \text{ K} < T < 43$ K: ferromagnetism/metamagnetism. $T > 43$ K: exchange-enhanced paramagnetism/metamagnetism. Temperatures (from upper to lower curve): 20 K, 30 K, 32.5 K, 35 K, 37.5 K, 40 K, 42.5 K, 55 K.

Figure 3 presents isothermal magnetization curves $M_T(H)$ in different temperature ranges. Below 33 K the curves are steep, with a horizontal saturation (no paraprocess) and minimal temperature dependence. Above 33 K, the magnetization curves display a minor indication of singularity. After initial steep increase, typical for ferromagnetic materials, the increase slows

down, forming a ‘dip’. Probably, at that field value, the field-assisted exchange interaction becomes strong enough to induce moments on the Co sites, and the resulting ferrimagnetism temporarily reduces the macroscopic magnetization. High enough fields restore ferromagnetic order. Figure 4 displays the magnetization curves transformed according to the Landau theory [18]. They do not display the partially linear behaviour as expected for second-order phase transitions. Consequently, the thermodynamic parameters cannot be evaluated, and only a change in curvature indicates the upper, second-order transition. Likely, the simple theory does not apply.

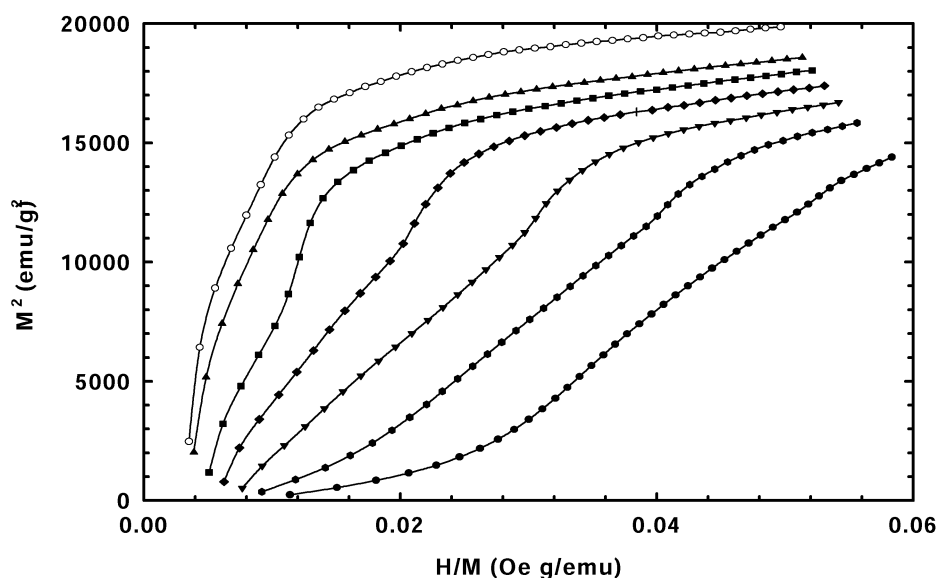


Figure 4. Magnetization curves transformed according to the Landau theory. Note the change of curvature at the second-order phase transition (≈ 40 K). Temperatures (from upper to lower curve): 20 K, 30 K, 32.5 K, 35 K, 37.5 K, 40 K, 42.5 K.

Figure 5 shows the temperature dependence of the specific heat $c_{P,H}(T)$, in zero, 7 T or 14 T applied fields. In zero field a slightly broadened first-order phase transition is observed. This is similar to the observations of Imai *et al* [19]. The peak is not fully symmetric. At the high temperature side a ‘foot’ extends to approximately 40 K. This feature can be interpreted as a smeared second-order transition from the ordering of the Er sublattice (compare [9]).

While for second-order transitions the specific heat discontinuity disappears with increasing external field (or at least becomes much less pronounced), in this case it is still well pronounced at 14 T, although the critical temperature—as expected—increases with increasing applied field. As the cobalt moment is not intrinsic, but induced in the d band by the exchange field due to the rare earth, at temperatures higher than the zero-field transition temperature (33 K), a magnetic field H must be applied to make cobalt magnetic in DyCo_2 , HoCo_2 and ErCo_2 . According to experimental findings in lower fields [11], this field depends linearly on the temperature difference, and the slope equals $2K/T$. On this basis, the transition is expected at ≈ 47 K for 7 T and at ≈ 61 K for 14 T. While the transition temperature in a 7 T applied field corresponds to 47 K with good approximation, it is clearly lower than 61 K for 14 T. It seems that high enough fields force the function to saturate.

At temperatures below 10 K the zero-field specific heat can be described by the expression $c_{P,H=0}(T) = aT^{-2} + \gamma T + \beta T^3 + \delta T^5$. We obtain $a = 0.13 \text{ J K mol}^{-1}$ which describes an upturn

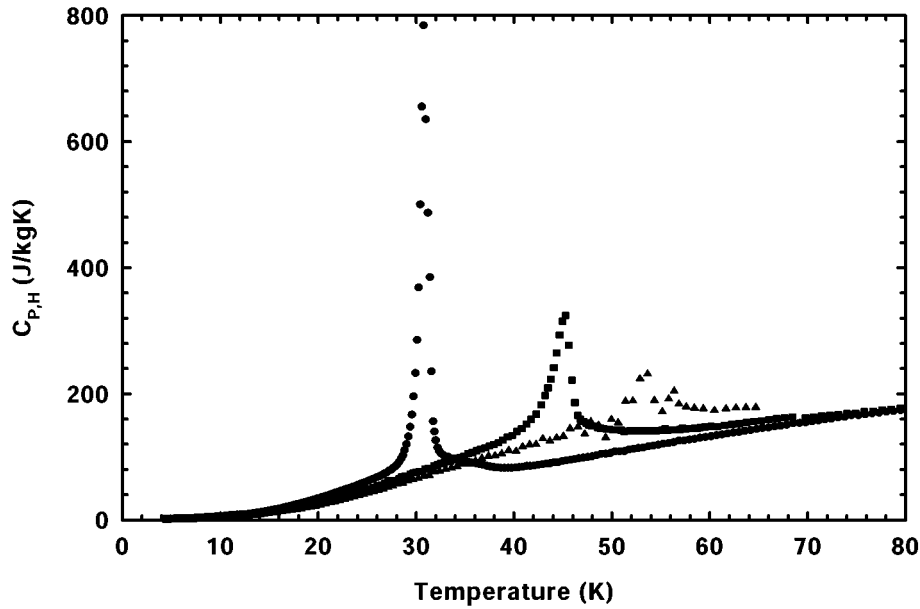


Figure 5. Temperature dependence of the specific heat capacity $c_{P,H}(T)$ in 0 T (●), 7 T (■), 14 T (▲) applied fields.

of the curve towards lower temperatures, presumably originating from the high-temperature tail of a Schottky anomaly (or a magnetic ordering) much below 1 K. Remarkable is the large linear coefficient $\gamma = 77 \text{ mJ mol}^{-1} \text{ K}^{-2}$ which may be due to an enhanced electronic density of states at the Fermi level or which may be mimicked by magnetic contributions. The remaining $\beta T^3 + \delta T^5$ are usually the lattice terms according to the Debye theory. We find $\beta = 6.5 \times 10^{-4} \text{ J mol}^{-1} \text{ K}^{-4}$ and a small $\delta = 1.9 \times 10^{-6} \text{ J mol}^{-1} \text{ K}^{-6}$, where β would be equivalent to an initial Debye temperature $\Theta_D(0) = 207 \text{ K}$. However, at temperatures far above the transition the Debye temperature is $\approx 300 \pm 20 \text{ K}$, a value somewhat larger than those found for $TbCo_2$ and $HoCo_2$ [20]. The low value of $\Theta_D(0)$ is obviously not representing the lattice properties but βT^3 is strongly enhanced by magnetic contributions. After subtraction of the lattice term as found for 100 K ($\Theta_D = 312 \text{ K}$) and the γT -term an estimate for the total magnetic specific heat $c_m(T)$ can be obtained. The total integrated magnetic entropy $S_m^{\text{cal}}(T) = \int c_m/T dT$ at $T = 100 \text{ K}$ is $\approx 2.6 R$, which is compatible with $R \ln(2J + 1) \approx 2.77 R$ and $J = 15/2$ for Er^{3+} , i.e. only the rare-earth moments contribute to the magnetic entropy [19].

Figure 6 gives the total entropies $S_{P,H}^{\text{cal}}(T) = \int c_{P,H}/T dT$ with or without a magnetic field, as integrated from the specific heat (i.e. calorimetric) data. The adiabatic temperature change ΔT_{ad} and the isothermal magnetic entropy change ΔS_T can be determined as the horizontal (parallel to the T axis) or vertical (parallel to the entropy axis) distance of the curves. Figure 7 shows the (magnetic) entropy change $\Delta S_m^{\text{cal}}(T, H) = S_{P,H}(T) - S_{P,H=0}(T)$ for 7 T and 14 T applied fields, as determined on the basis of calorimetric measurement. The field has far more impact on the width of the peak than on the peak amplitude itself. This is typical for metamagnetic transitions: the maximal entropy change is determined by the critical field, any field increase beyond that does not influence the amplitude significantly. However, the critical field increases with temperature, thus higher applied field allows the material to be above the critical field in a wider range of temperature. Figure 7 also displays the field

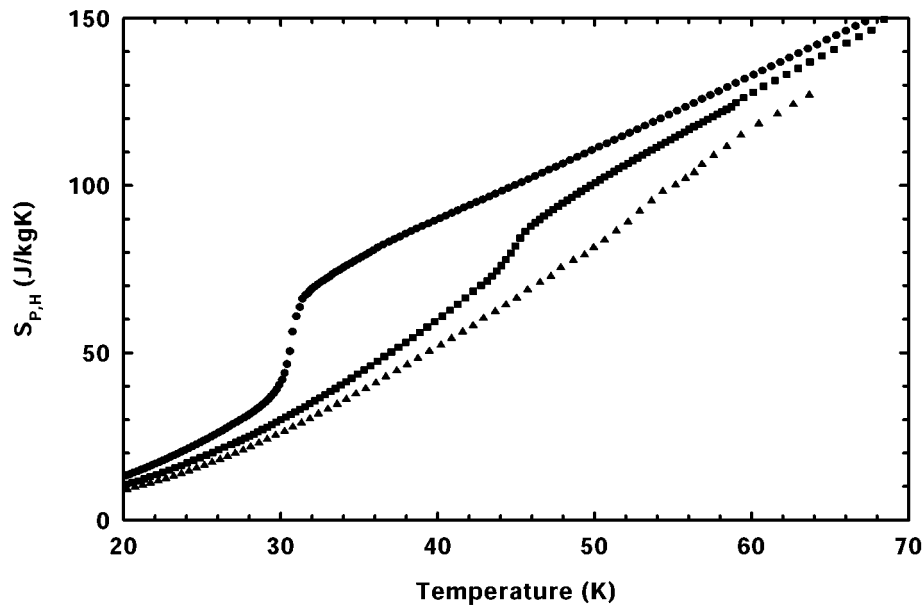


Figure 6. Temperature dependence of the total entropy $S_{P,H}^{\text{cal}}(T)$, in 0 T (●), 7 T (■), 14 T (▲) applied fields; as integrated from specific heat data (figure 5).

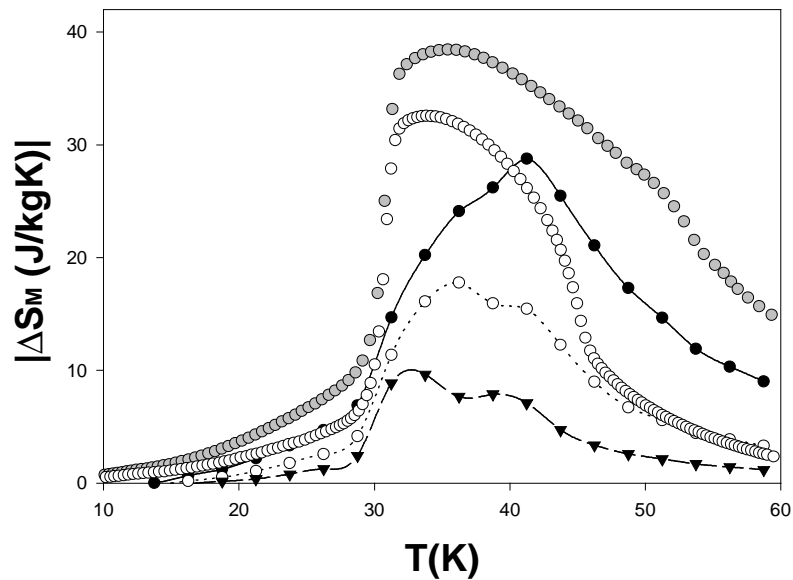


Figure 7. Comparison of the magnetic entropy change $\Delta S_m(T)$ obtained from magnetization curves (ΔS_m^{mag}) in applied fields of 1.75 T (-▼-), 3.5 T (-○-), 7 T (-●-) or from calorimetric measurements (ΔS_m^{cal}) in 7 T (○) and 14 T (shaded circles) applied fields, respectively.

and temperature dependence of the magnetic entropy change $\Delta S_m^{\text{mag}}(T, H)$, as calculated from magnetization measurements. *The temperature of the maximum and the shape of the curves, calculated from magnetic or thermal data, do not agree as well as for second-order transitions*

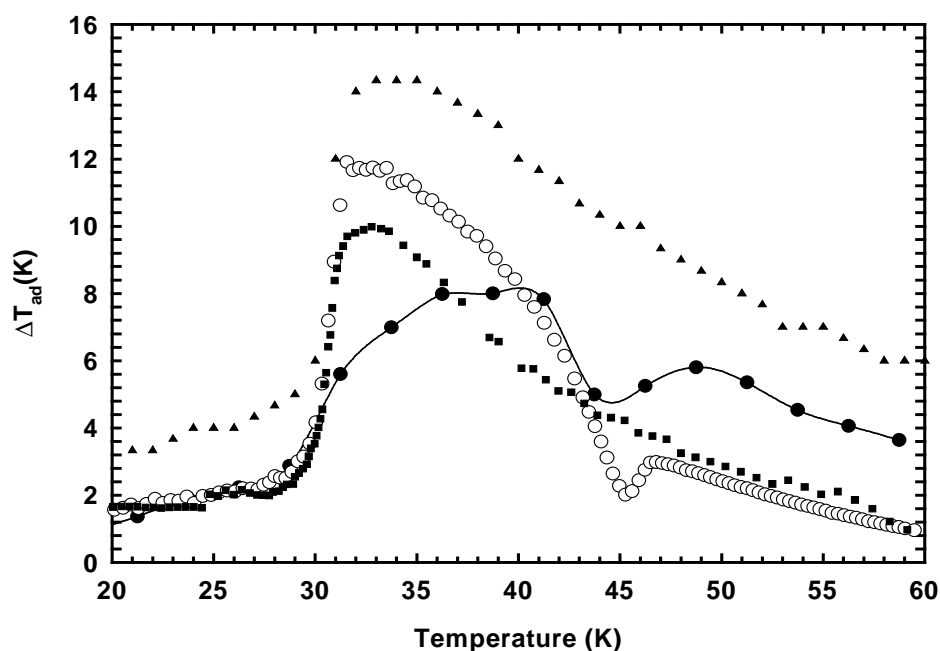


Figure 8. Adiabatic temperature change ΔT_{ad} , as calculated via different methods from the magnetic entropy change $\Delta S_{\text{m}}^{\text{mag}}$ and $c_{P,H=7\text{ T}}$ (-●-), from $\Delta S_{\text{m}}^{\text{cal}}$ and $c_{P,H=7\text{ T}}$ (○), from the distance between $S_{P,0}^{\text{cal}}$ and $S_{P,H=7\text{ T}}^{\text{cal}}$ (■) and from the distance between $S_{P,0}^{\text{cal}}$ and $S_{P,H=14\text{ T}}^{\text{cal}}$ (▲).

[17]. Also, the shape of the entropy curves calculated from magnetization data undergoes a significant transformation with increasing field. The unexpected discrepancy, including the field dependence of the shape, can be interpreted by taking into consideration the specific features of first-order/metamagnetic transitions and magnetoelastic coupling to lattice degrees of freedom. Magnetoelastic coupling is quite strong in the RCO_2 as becomes obvious from the large thermal expansion anomaly in Y-diluted ErCo_2 [9].

Above 33 K, the temperature of the metamagnetic transition in the cobalt sublattice is field dependent. In isothermal curves, the transition results in a decrease of the susceptibility or even magnetization. This point shifts toward higher fields with increasing temperatures. Thus when calculating dM/dT , there is always a field region with unusually high dM , because one of the curves is below, the other above the transition. This explains the spike at a field-dependent temperature in the entropy curves. However, as the entropy change in the cobalt sublattice cannot be described by the localized model [20], the change of the macroscopic magnetization cannot be considered proportional to the change of the order parameter, consequently the calculation does not reflect correctly the true entropy change. In other words, the spike has to be regarded as an artefact. In high field, the apparently reduced magnetic entropy change on the low temperature side can be interpreted as the result of slower saturation due to the metamagnetic transition in the Co sublattice and the prevailing ferrimagnetic order. As the macroscopic magnetization apparently decreases, although the true order parameter is actually increased, a ‘lack’ of entropy is experienced. In low fields, the magnetic fluctuations of the system are enhanced by the field, instead being suppressed as in usual spin-fluctuation compounds. In a strong magnetic field limit the fluctuations are considered to be suppressed

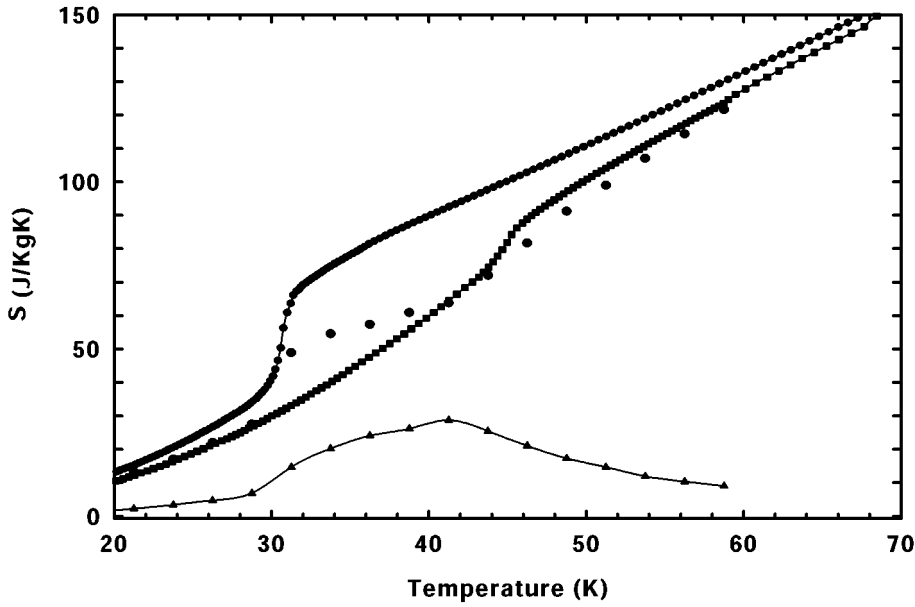


Figure 9. Figure illustrating the ambiguity of graphical adiabatic temperature difference determination. Continuous curves correspond to the total entropy $S_{P,H}^{\text{cal}}(T)$ at $H = 0$ or $H = 7$ T, as calculated from the specific heat. The peak corresponds to $\Delta S_m^{\text{mag}}(T)$ from magnetization measurements. (●) $S_{P,H=0}^{\text{cal}}(T) - \Delta S_m^{\text{mag}}(T) \neq S_{P,H}^{\text{cal}}(T)$, in contrast to the agreement as found for second-order transitions.

and $(\partial M/\partial T)_H$ is expected to become negative. Thus, the low temperature magnetization process in these systems should have an unusual nonlinearity, followed by itinerant electron metamagnetism, a first-order field-induced transition [21]. On the high temperature side, in contrast, the metamagnetic transition in the region of exchange-enhanced paramagnetism [22] displays higher changes in macroscopic magnetism than in the order parameter, and as a result an apparent ‘excess’ is seen in the entropy. The problems are more pronounced in the case of the adiabatic temperature change. Figure 8 compares adiabatic magnetocaloric effect ΔT_{ad} as calculated from the magnetically or calorimetrically determined magnetic entropy change, using the field dependent specific heat in the latter case, as described in an earlier publication [17]. The main reason for the disagreement is the strong (non-negligible) dependence of the specific heat on the applied magnetic field. As a result of the sharp transition, the discontinuity of the specific heat curves does impact the calculated adiabatic temperature change. Unlike for second-order transitions, the adiabatic temperature change ΔT_{ad} calculated from calorimetric data does not agree with calculations based on simple models. Increasing the applied field to 14 T results in a significant broadening of the adiabatic temperature change curve, while the increase in amplitude is much slower than linear with field H for $\Delta T_{\text{ad}}(H)$.

For simple second-order transitions [17,23] the thermally or magnetically obtained magnetic entropy change agrees well, except maybe for an additive integration constant; for which the correction is justified and straightforward [17,24].

As figure 7 displays, the difference for this case is more complicated than an additive constant in the magnetic entropy difference $\Delta S_m^{\text{mag}}(T, H)$. Figure 9 illustrates the problem in another representation. For second-order phase transitions, the difference $S_m^{\text{cal}}(H = 0) - \Delta S_m^{\text{mag}}(H) = S_m^{\text{cal}}(H)$ for any given temperature. In the case of ErCo_2 the curves

are different and might become more different in the case of a more abrupt transition. The decision of which curves to use when calculating a reliable ΔT_{ad} can be best justified by direct measurement.

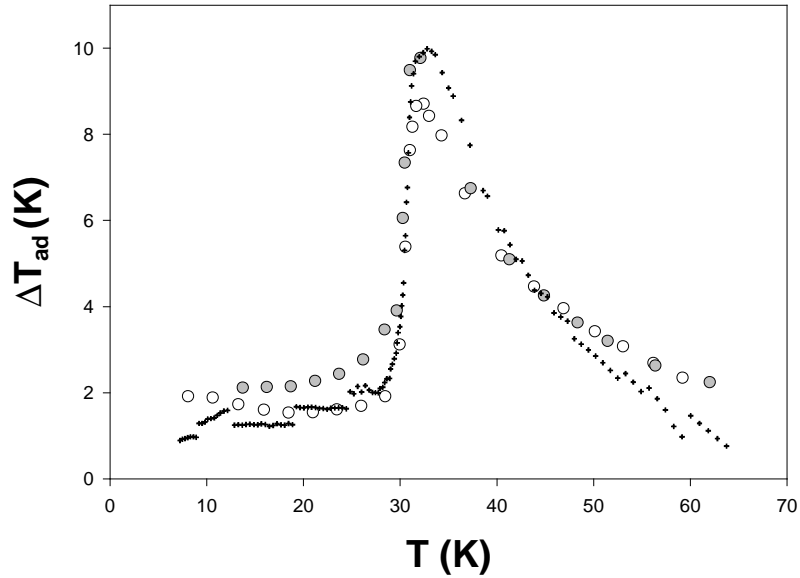


Figure 10. Adiabatic temperature change $\Delta T_{\text{ad}}(T)$ measured or calculated (based on calorimetric measurements) for slightly different ErCo_2 samples. Circles represent repeated direct measurements on sample B, proving the experiment's good reproducibility. Results represented by crosses are calculated from specific heat measurements performed on sample A.

Figure 10 shows direct measurements of the adiabatic magnetocaloric temperature change ΔT_{ad} on sample B. In spite of the presence of a minor second phase in this sample and the resulting difference in magnetic properties [2], the agreement with the adiabatic temperature change calculated from specific heat measurements is very good. This proves the known fact that thermal properties are less structure sensitive than magnetization curves.

On this basis, firstly, the full equation (1) has to be taken into account, i.e. the coupling of the magnetic system to electronic and lattice degrees of freedom. Secondly, *using the Maxwell relations to evaluate the magnetic entropy change over the entire temperature or field range might not be appropriate in first-order transitions*. Of course, the Maxwell relations are mathematical equations, and, as such, are correct. It must be investigated, though, whether in the *specific magnetic system* they are still valid. When calculating the magnetic energy of a solid from the macroscopic magnetization, the following assumptions are made:

- (i) M is a single-valued function of H ;
 - (ii) M reflects the changes of the magnetic order parameter only, i.e. excludes collective reorientation of spins, like domain wall displacements, spin reorientation transitions, etc.
- The exchange interaction is assumed to be constant, not influenced by the lattice in any respect.

In a metamagnetic transition or in a first-order transition, M is *not* a single-valued function of H , and its macroscopic change might be far more than the change in the order parameter. If we assume a material in which all spins of one sublattice change direction collectively, the

magnetization change might be significant, while the order parameter might change or not, but the entropy change might be very small or even zero. A large magnetic entropy change ΔS_m^{mag} as obtained from magnetization measurements $M_T(H)$ might be only a numerical/experimental artefact.

For economic reasons it might seem advantageous to classify candidate materials for magnetic refrigeration by the faster/less costly magnetic methods first, and perform the more complicated/costly calorimetric measurements only on samples passing the first test. This method proved reliable for materials with second-order transitions [23, 25]. With first-order transitions, not only the specific heat, but the entropy also displays a discontinuity at the transition [15]. The macroscopic magnetization is no longer a single-valued, continuous function of the order parameter. Although the Maxwell relations remain valid as mathematical formulae, the physics justifying the integration over H becomes questionable: the paraprocess is no longer a good approximation to describe the increase of the magnetization. Simultaneously, the simplified equation to calculate the adiabatic temperature change from the magnetic entropy change [17, 25] loses its validity just as well. To obtain the simplified formula, the dependence of the specific heat on applied field should be negligible as compared to the temperature dependence of the magnetization, which is wrong in certain field or temperature ranges for first-order magnetic transitions. In addition magnetoelastic coupling may lead to a further complication of the behaviour of the 'magnetic' entropy difference and thus to a modification of the value of ΔT_{ad} .

4. Conclusions

The intermetallic compound ErCo_2 was studied near its first-order magnetic transition temperature; via magnetization and specific heat measurements. The results confirm the double transition in ErCo_2 , as observed earlier [3, 9] and predicted theoretically [11] and prove the presence of metamagnetism at higher temperatures. Unlike the case in second-order transitions, the magnetic entropy changes obtained from magnetic or calorimetric measurements do not agree. It was shown that this is a consequence of the first-order/metamagnetic transition and the related singularity of the magnetization curves, which cannot be separated by mathematical means, when calculating the magnetic entropy change from magnetization curves. For this reason, in samples with first-order magnetic transitions, magnetic measurements and zero-field specific heat data alone do not allow for a reliable prediction of magnetocaloric performance.

Acknowledgments

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