Conference Paper

Features of Magnetocaloric Effect in $Er(Co\text{-}Fe)_2$ Laves phases

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Abstract

In this work the results of measurements of heat capacity (C_P) and magnetocaloric effect (MCE) in $Er(Co_{1-x}Fe_x)_2$ system in the concentration range $0.07 \leq x \leq 0.80$ are presented. Phase composition was controlled by X-ray difraction analysis. Heat capacity was measured in the temperature range 77-320 K. MCE has been studied within the temperature range 5-670 K in magnetic fields up to 70 kOe. It was found that Fe concentration increase caused the table-like (plateau) MCE temperature dependence for both magnetic entropy change date and direct ΔT-effect measurements independently on Fe concentration. The possible reasons of such behavior are discussed.

Keywords: magnetic properties, magnetocaloric effect, magnetic entropy change, Laves phase, heat capacity

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1. Introduction

RCo_2 type binary compounds (R are the heavy rare earth elements) exhibit high magnetocaloric effect (MCE) or ΔT-effect at their magnetic phase transition temperatures [1]. During magnetic properties and MCE studies of quasibinary $R(M_{1-x}Fe_x)_2$ (M = Ni, Co) ferrimagnets, it was found that a partial Co or Ni replacement by Fe caused a significant MCE in a wide temperature range lower than Curie point (T_C) [2]. Such their ability is very attractive for magnetic refrigeration.

Our recent MCE measurements for some $Ho(Co_{1-x}Fe_x)_2$ [2] compounds in the relatively narrow range ($0 \leq x \leq 0.20$) confirmed that results and allowed suggesting the reasons of MCE peak widening to the temperature range lower than their T_C.

For more deep understanding of magnetic and MCE mechanisms formation in $Er(Co\text{-}Fe)_2$ compounds we have studied the magnetocaloric properties of such systems with the Co substitution by Fe in the concentration range $0.07 \leq x \leq 0.80$.

2. Methods

$Er(Co_{1-x}Fe_x)_2$ alloys were melted in induction furnace with argon protective atmosphere or in electric arc furnace under a pure helium protection. An excess of rare earth metal (~2 wt. %) was added to the starting compositions to prevent the formation of Co-rich

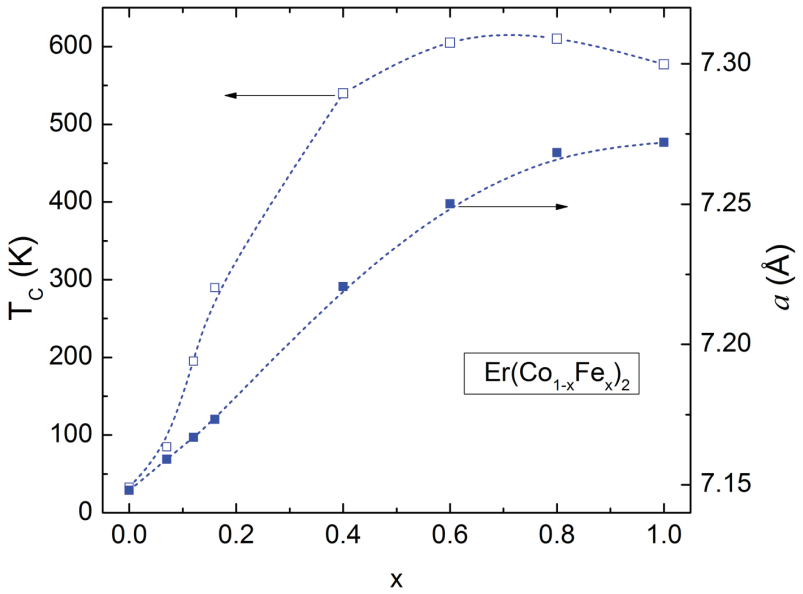

Figure 1: Dependences of crystal lattice parameter (*a*) and Curie point (T_C) on iron concentration (x). The data for $ErCo_2$ and $ErFe_2$ are taken from [3-5].

phases. A homogenizing annealing of alloys was made in a vacuum furnace at 1220 K during 7-32 hours. The structure of the samples was determined by X-ray diffraction (D8 Advance, Bruker) with Cu K_α radiation source. Diffraction patterns were analyzed by Rietveld method using the "Fullprof" software.

Magnetic properties were measured using both a SQUID-magnetometer (MPMS-XL-7, Quantum Design) in the magnetic field up to 70 kOe and a vibrating sample magnetometer (7407, Lake Shore Cryotronics) in the temperature range 450-660 K under a magnetic field up to 10 kOe. Heat capacity was measured at zero magnetic field using adiabatic calorimeter with the relative error of ± 0.6 %. Direct MCE measurement (ΔT-effect) was carried out using MagEq MMS SV3 experimental apparatus in the magnetic field 17.5 kOe.

3. Results

Analysis of the X-ray diffraction data at room temperatures showed that all samples contained mainly the 1:2 phase. The crystal lattice calculation parameter (*a)* are presented in Figure 1. The temperatures of magnetic transitions (T_C) for the studied samples (Fig. 1) were determined from the positions of the dM/dT peaks on the temperature axis, taken from the specific magnetization temperature dependencies (M(T)) in the magnetic field of 0.1 kOe.

Taking into account the results of [5-7], it is possible to infer that the nonlinear $T_C(x)$ dependences correlate with the mean magnetic moment of the 3d-ions subsystem $\mu_d(x)$ in these compounds. Non-monotonic dependence $T_C(x)$ is correlated with the dependence of the magnetic moment of the d-sublattice vs. concentration iron $\mu_d(x)$. Thus, we can conclude that d-d-exchange interaction dominates in these systems for the whole Fe-concentration range except the region with $x \sim 0$ only.

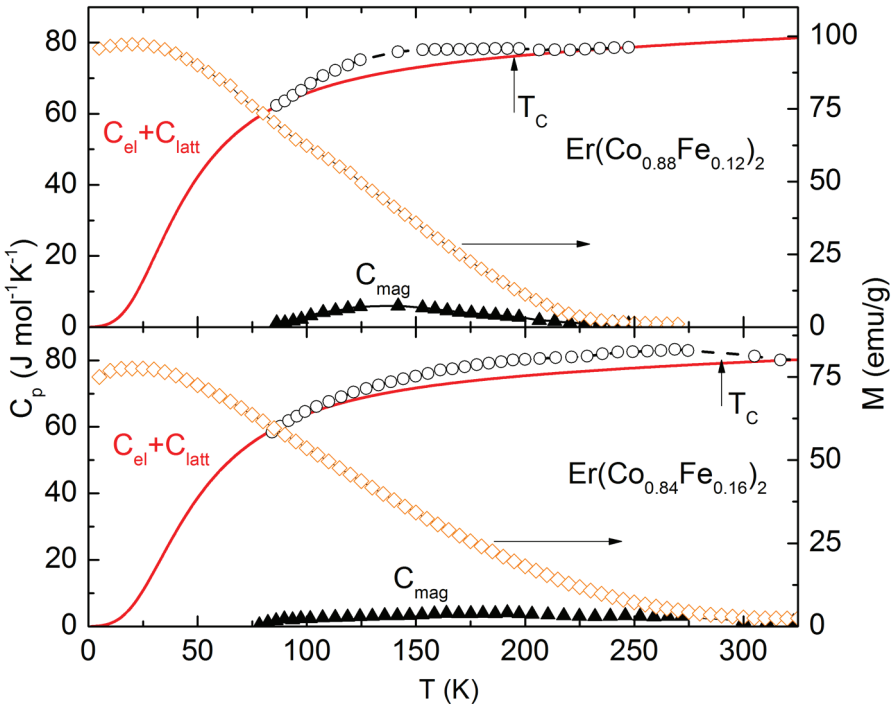

Figure 2: On the left axis: $C_P(T)$ - experimental data (open symbols), C_{el} + C_{latt} - calculated lattice and electronic contributions (dashed line), C_{mag} - magnetic contribution (filled symbols). On the right axis: specific magnetization temperature dependences at 5 kOe.

3.1. Heat Capacity

In Figure 2 the experimental data on heat capacity temperature dependences $C_P(T)$ are given for some studied samples. The algorithm of electron-lattice (C_{el}+C_{latt}) and magnetic (C_{mag}) contributions calculations is presented in Ref. [2]. For $Er(Co_{0.88}Fe_{0.12})_2$ sample in the vicinity of T_C point the maximum of $C_P(T)$ dependence is observed in a wide temperature range. In the sample with a higher Fe concentration the maximum of $C_P(T)$ dependence is observed in a wider temperature interval.

Such spread of $C_{mag}(T)$ maximum reflects the emergence and existence of specific magnetic disorder in a wide temperature range, which also is reflected on the specific magnetization temperature dependences - M(T). It is worth noting that M(T) dependences of $Er(Co_{1-x}Fe_x)_2$system samples differ from the Weiss type and all have the deflection with temperature rise, which correlates with $C_{mag}(T)$ data.

3.2. Magnetocaloric Effect

The existence of magnetic disorder in studied compounds inferred from the analysis of temperature dependences of heat capacity should be considered as a magnetic entropy change (ΔS) in a wide temperature range. In Figure 3, temperature dependences of magnetic entropy change ΔS(T) are presented. The ΔS(T) value was calculated using the formula from Ref. [8].

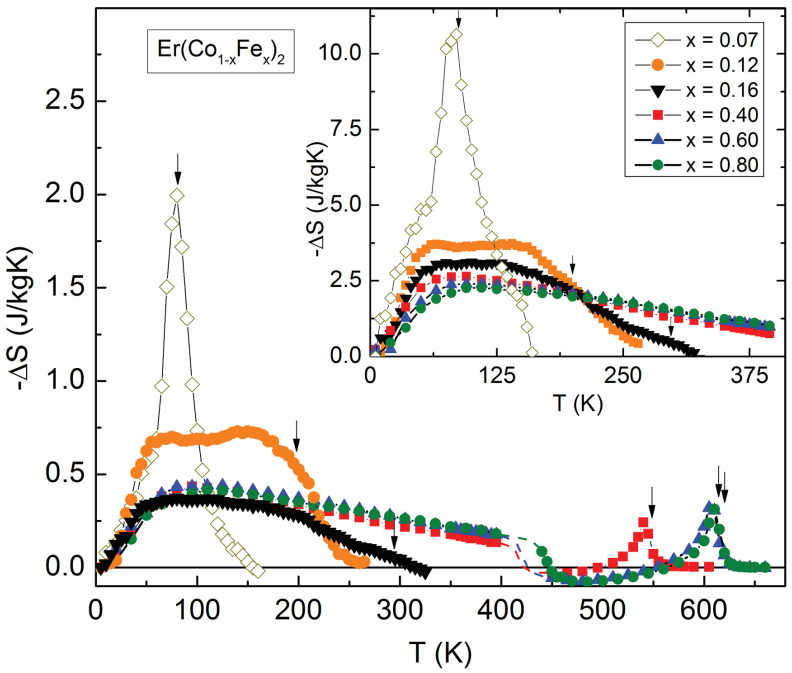

Figure 3: ΔS(T) in magnetic fields (0-10) kOe. Inserts: ΔS(T) in magnetic fields (0-70) kOe. Arrows indicate the T_C point. The dash line – extrapolation.

It is seen that the magnetic disorder causes the appearing of table-like (plateau) MCE at the $T < T_C$. For compounds with $x \leq 0.20$ this plateau is merged with the MCE peak at T_C point, thus presenting only one wide common peak. At the higher Fe concentration, the MCE peak caused by the magnetic phase transition at T_C point is detached from the plateau area, which connected with some magnetic disorder in R-sublattice. The same picture of plateau-like ΔS(T) dependence has been observed in Ref. [9] for $ErFe_2$.Besides, for the $Er(Co_{1-x}Fe_x)_2$ samples with $x \geq 0.40$ the magnetization compensation point was found in Ref. [4] accompanied by the reversed MCE.

Our the ΔS(T) experimental dependences for the magnetic field change of 10 kOe are correlated with the direct ΔT-effect measurements data for the adiabatic external magnetic field change of 17.5 kOe (Fig. 4).

4. Conclusion

We found that Fe concentration increase cause the following magnetothermal and magnetocaloric properties changes in the studied systems:

1. A heat capacity maxima disappearing at T_C point and emergence of magnetic contribution to a heat capacity in a wide temperature range lower than this point;
2. The plateau-like MCE temperature dependence for both magnetic entropy change data and direct ΔT-effect measurements independently on Fe concentration.

To our mind, the mentioned MCE features in $R(Co_{1-x}Fe_x)_2$ intermetallics originate from the specific magnetic state of R-ions sublattice which belongs according of Belov

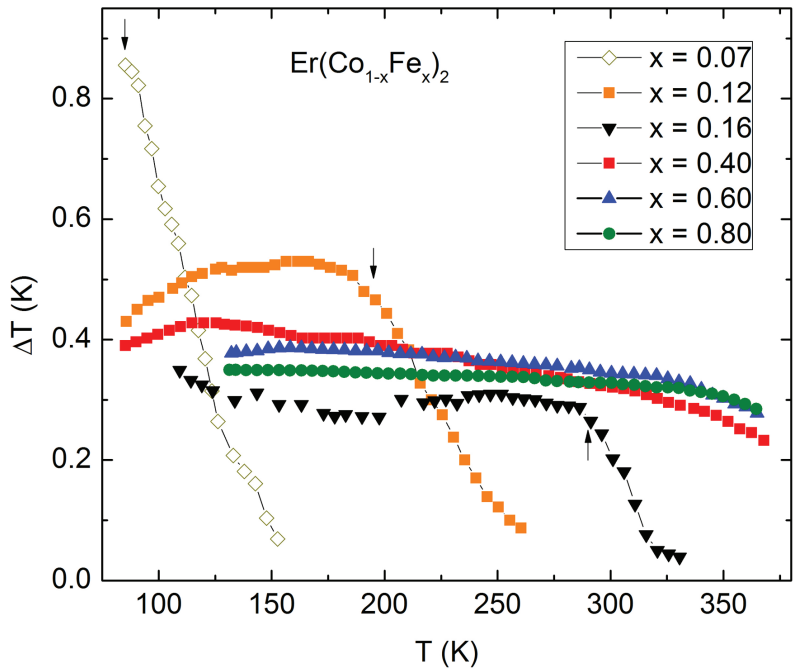

Figure 4: Temperature dependencies of ΔT-effect. Arrows indicate the T_C point.

classification [10] to a "weak" type. Due to that reason, the R-sublattices are partially magnetically disordered in the range o K – T_C (state similar for paramagnet), but able to give a great response to the external magnetic field. Another possible reason is the sperimagnetic structure formation in R-sublattices due to the local electric crystal field change acting on R-ion from the Fe-ion neighbors; in other words, the deflection of R-ions magnetic moments out from the global easy axis. In that case, the external magnetic field aligns them, which produces the specific contribution to entropy. Found experimental data are very important for the MCE mechanism origin understanding and for design of novel and potential magnetic refrigerant materials working at room temperature.

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References

[1] A. Gschneidner Jr., V. K. Pecharsky, and A. O. Tsokol, Recent developments in magnetocaloric materials, *Reports on Progress in Physics*, **68**, no. 6, 1479–1539, (2005).

[2] M. Anikin, E. Tarasov, N. Kudrevatykh, A. Inishev, A. Zinin, and A. Teplykh, Pirogov A: Magnetic structure and magnetocaloric properties of, *Phys. Procedia*, **75?**, 1198–1206, (2015).

[3] M. I. Bartashevich, H. Aruga Katori, T. Goto, H. Wada, T. Maeda, T. Mori, and M. Shiga, Collapse of the itinerant Co moment in Er1-xLuxCo2 by the application of high magnetic fields, *Physica B: Condensed Matter*, **229**, no. 3-4, 315–320, (1997).

[4] AV. Andreev, AV. Derjaguin, MS. Zadvorkin, and VN. Moskalev, Sinitsin EV: Influence of 3d-metal on the magnetic properties of quasi-binary intermetallic compounds of rare-earth Er(Fe1-xCox)2., Phys. Metals Metallogr, *Phys. Metals Metallogr*, **59**, 481–488, (1985)., in Russian.

[5] X. B. Liu, Z. Altounian, and D. H. Ryan, Moment variation in Er (Co1-x Fex) 2 Laves phase: Magnetic measurements and Mössbauer spectroscopy study, *Journal of Applied Physics*, **105**, no. 7, Article ID 07E119, (2009).

[6] E. Burzo, Magnetic properties and resonance studies of some pseudobinary gadolinium or yttrium compounds, *J. Phys. Colloque*, **40**, C5–184, (1979).

[7] F. Pourarian, W. E. Wallace, and S. K. Malik, Magnetic behavior of Laves phase RCo2-xFex (R = Ho, Er) compounds and their hydrides, *Journal of Magnetism and Magnetic Materials*, **25**, no. 3, 299–306, (1982).

[8] K. A. Gschneidner Jr. and V. K. Pecharsky, Magnetocaloric materials, *Annual Review of Materials Science*, **30**, 387–429, (2000).

[9] E. Burzo, I. G. Pop, and D. N. Kozlenko, Magnetic and magnetocaloric properties of some ferrimagnetic compounds, *Journal of Optoelectronics and Advanced Materials*, **12**, no. 5, 1105–1113, (2010).

[10] K. P. Belov, Ferrimagnets with a weak magnetic sublattice, *Uspekhi Fizicheskikh Nauk*, **166**, no. 6, p. 681, (1996).