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Magnetic structure and magnetocaloric properties of $Ho(Co_{1-x}Fe_x)_2$ quasibinary intermetallic compounds

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Abstract
A study of crystal and magnetic structures, heat capacity, magnetic and magnetocaloric properties of $Ho(Co_{1-x}Fe_x)_2$ (with increasing x from 0 to 0.2) intermetallic compounds has been undertaken. Phase composition was controlled by X-ray diffraction analysis. Neutron diffraction experiment was performed at temperatures of 78 and 293 K. Magnetic properties were measured within the temperature range 5÷325 K in magnetic fields up to 70 kOe. It was shown that considerable maximum broadenings on the temperature dependence of magnetic entropy change is observed with iron concentration increase. The avarage magnetic moment of Ho ions in their sublattice decreases from 10 μ_B for $HoCo_2$ to 9 μ_B for $Ho(Co_{0.8}Fe_{0.2})_2$ that can be connected with the existence of the umbrella-like (canting) magnetic structure in Ho-sublattice.

Keywords: intermetallics; magnetocaloric effect; heat capacity; magnetic entropy change; magnetic properties; neutron powder diffraction

1 Introduction

RT_2 type intermetallic compounds (where R - rare earth, T = Fe, Co, Ni) - Laves phases with a cubic crystalline structure intensively studied for more than 3 decades, primarily because of a series of them based on Fe have a giant magnetostriction values (Clark, 1979). The first magnetocaloric effect (MCE) studies in RT_2 compounds were carried out on the samples of binary alloy $HoCo_2$ (Nikitin & Tishin, 1991) where the significant MCE has been found at the temperature of magnetic phase transition. Therefore these compounds from that time are considered as a potential materials for their applications in a magnetic refrigeration technology (Foldeaki, et al., 1988). Besides the MCE

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study allows to detecting the magnetic structure changes in the materials, so it is a useful tool for its finding and characterization.

At the MCE studies in quasibinary compounds: $Ho(Ni_{1-x}Fe_x)_2$ (Singh, et al., 2005), $Tb(Ni_{1-x}Fe_x)_2$ (Singh, et al., 2006), $Er(Co_{1-x}Fe_x)_2$ (Liu & Altounian, 2008), $Tb(Co_{1-x}Fe_x)_2$ (Halder, et al., 2010), $Ho(Al_{1-x}Fe_x)_2$ (Mican, et al., 2013) and $Dy(Co_{1-x}Fe_x)_2$ (Anikin, et al., 2015b) it was found that the Fe introduction leads to the abnormal MCE temperature dependences having the table-like MCE peak with its width broadening under the Fe concentration rise. Recently we have prepared $Ho(Co_{1-x}Fe_x)_2$, compounds (Anikin, et al., 2015a) and found the MCE presence in these compounds for more wider temperature range than it was shown in (Singh, et al., 2005; Singh, et al., 2006; Liu & Altounian, 2008; Halder, et al., 2010). The MCE peak width was comparable with those found in (Mican, et al., 2013; Anikin, et al., 2015b), but its absolute value was much higher. In this paper we present the results of magnetic structure and magnetocaloric properties study of $Ho(Co_{1-x}Fe_x)_2$ compounds over wider Fe concentration range having the aim to clarify the reasons of abnormal MCE appearing and its evolution on Fe concentration rise.

2 Experimental details

$Ho(Co_{1-x}Fe_x)_2$ alloys (x = 0, 0.04, 0.07, 0.12, 0.20) were melted in induction furnace using a quartz crucible with an argon protective atmosphere. An excess of Ho (2 wt. %) was added to the starting compositions to prevent the formation of Co-rich phases. A homogenizing annealing of alloys was made in a vacuum furnace at 1220 K during six hours. Phase composition control and crystalline structure studies were carried out by means of X-ray diffraction technique (diffractometer Bruker D8 Advance) with Cu Kα-radiation source. Neutron diffraction experiment was carried out with the diffractometer D-2, installed on reactor IVV-2M, Zarechny, Russia. The neutron wave length of an incident beam was 1.805 Å. Calculations of neutron powder diffraction (NPD) patterns were performed using "Fullprof" program (Rodríguez-Carvajal, 1993).

Magnetic phase analysis and magnetization curves measurements were made using SQUID–magnetometer MPMS-XL-7 EC (Quantum Design) in the temperature range from 5 K to 325 K in magnetic field up to H = 70 kOe. Heat capacity was measured at zero magnetic field using adiabatic calorimeter in the temperature range 77÷315 K with an error of ± 0.6 %. Direct MCE measurement (ΔT-effect) was carried out with the help of MagEq MMS SV3 experimental apparatus in the temperature range 85÷370 K in the magnetic field of H = 17 kOe.

3 Results and discussion

Analysis of the room temperature X-ray diffraction data showed that all samples within the study were single-phase. The 1:2 composition phase had a cubic structure of $MgCu_2$ type with Fd3m space group and lattice parameter a increasing linearly from 7.1594(2) Å to 7.1830(2) Å up on x rise from 0 to 0.12.

Samples were confirmed to contain only 1:2-phase by specific magnetization temperature dependence (M(T)) measurements at the external

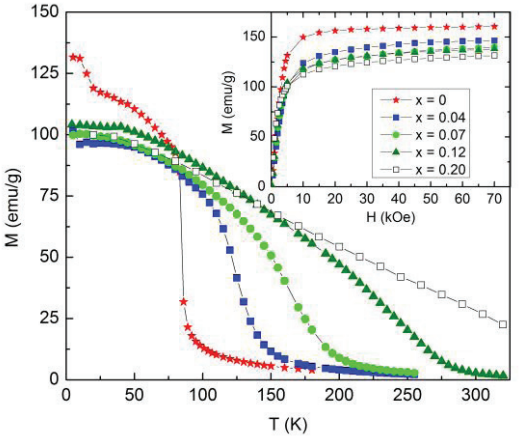

Figure. 1: Specific magnetization temperature dependences of $Ho(Co_{1-x}Fe_x)_2$ compounds in the external magnetic field of 5 kOe. Inset - M(H) at 5 K

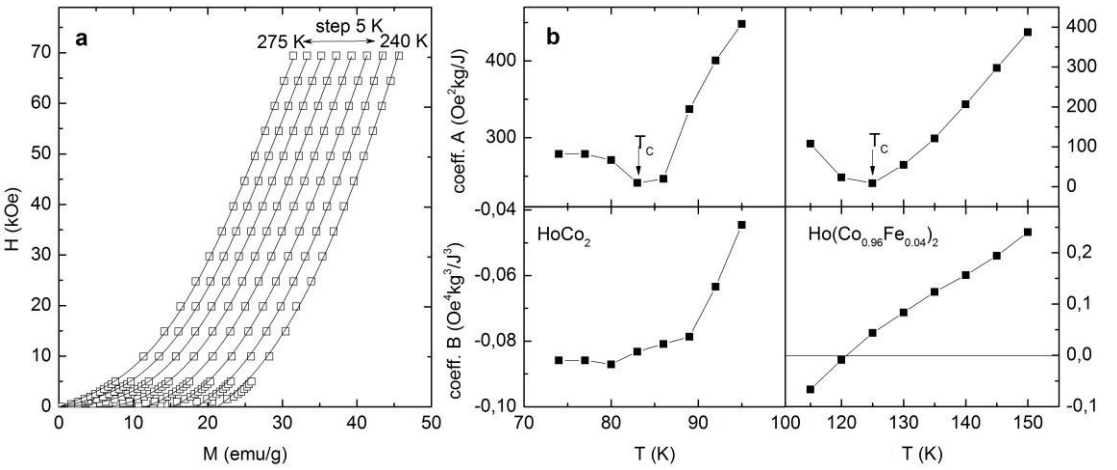

Figure. 2: a) Magnetization M(H) of $Ho(Co_{0.88}Fe_{0.12})_2$ at different temperatures. The solid lines represent the fits by Eq. (2); **b)** Temperature dependence of Landau coefficients for two selected samples

magnetic field H = 5 kOe (Figure. 1). A sharp magnetization fall on M(T) for $HoCo_2$ at T=15 K originates from the magnetic spin orientation transition in this compound (the easy axis (EA) reorientates from [110] to [100] crystallographic direction) with T rise (Gignoux, et al., 1975). This EA orientation change is explained by the competition of 4-th and 6-th order crystal electric field contributions to the magnetic anisotropy energy. No other anomalies on M(T) curves for these compounds are observed.

3.1 Magnetic behavior near T_C

The temperatures of magnetic-transitions for the samples with x = 0.00, 0.04, 0.07 and 0.12 were inferred to be 83, 125, 160 и 256 K respectively. They were determined from the position of the dM/dT peaks on the temperature axis.

In order to determine the magnetic transition type which occurs with Fe substitution we have employed the Inoue–Shimizu s–d model (Shimizu & Inoue, 1982; Bromme, 1989), which has been proven to be suitable for determination of magnetic transitions in RCo_2 compounds. In this model, a Landau expansion of magnetic free energy up to the sixth power of total magnetization M is used:

$$F = {}^1\!/_2\, A(T)M^2 + {}^1\!/_4\, B(T)M^4 + {}^1\!/_6\, C(T)M^6 + \cdots - MH \quad (1)$$

The nature of the transition is determined by the dependence of F on the magnetization and temperature. In the thermal equilibrium conditions $(\partial F/\partial M) = 0$, the equation of state is derived as:

$$H = A(T)M + B(T)M^3 + C(T)M^5 \quad (2)$$

Fitting the experimental data (Figure. 2a) by this dependence, we inferred the thermal coefficient values and their temperature dependences - A(T), B(T) и C(T) for compounds with x = 0.00 and 0.04 (plotted in Figure. 2b for A and B coefficients). Their analysis allows to determining the type of magnetic transition at the Cuire point. As it seen, for $HoCo_2$ the A(T) curve at this temperature has a distinct minimum but the B(T) value is negative. So, in the accordance with Landau theory this combination testifies the first order magnetic transition type in $HoCo_2$. If the B(T) > 0, the transition type becomes the second order which evidently takes place in all substituted compounds. Thus, on the basis of the analysis of the obtained experimental data it is possible to claim, what even the small Co replacement with Fe (4 %) leads to change of phase transition type in these compounds system from the first to the second order type.

3.2 Magnetic moment

On an insert of Figure. 1 the magnetization curves (M(H)) of the studied samples are presented at the temperature of 5 K. A magnetic moment (in Bohr magneton - μ_B) was calculated for a formula unit - M_{FU} from M(H) data when M value is taken for H = 70 kOe. The M_{FU} decreases from 8.12 to 6.63 μ_B, at Fe concentration increase from x = 0.00 to x = 0.20. It is unambiguously impossible to define the magnetic moment of d-sublattice from these data as the values of the magnetic moment of Ho-ions and magnetic structure of the Ho–sublattice are unknown. However, if to accept the Burzo's data (Burzo, 1979), on 3d - sublattice magnetizations in $Gd(Co_{1-x}Fe_x)_2$, it is possible to define the Ho-ion average magnetic moment value in the studied compounds Taking in the consideration also the global antiparallel 3d- and R-ion sublattice magnetizations it can find out that the magnetic moment of Ho ions in their sublattice decreases from 10 μ_B for $HoCo_2$ (that corresponds to magnetic moment of a free Ho^{3+} ion) to 9 μ_B for $Ho(Co_{0.8}Fe_{0.2})_2$ (Figure. 3), that can be connected with the existence of the umbrella-like (canting) magnetic structure in Ho-sublattice.

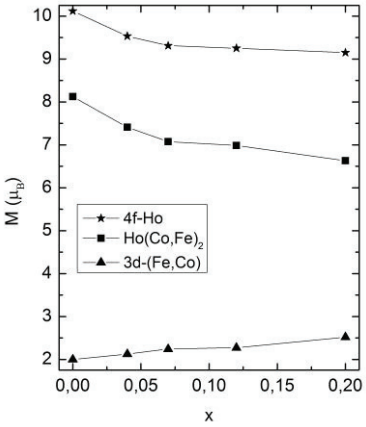

Figure. 3: Magnetic moments of formula unit Ho- and 3d- ions (average) on Fe concentration (x) in $Ho(Co_{1-x}Fe_x)_2$ system at 5 K

Magnetization curves of isotropic Fe-introduced compounds do not reach the saturation even in the field of 70 kOe (an insert of Figure. 1). This fact can testify, both the considerable magnetic crystallographic anisotropy existence and a possible noncollinearity of Ho- magnetic moments orientations inside the Ho- sublattice.

For determination of the main reason for such M(H) behavior we performed the M(H) measurements for isotropic and oriented powder samples of $Ho(Co_{0.8}Fe_{0.2})_2$ compound. Comparison of two curves, showed that their courses are almost identical that can confirm the suggestion of noncollinear magnetic structure farmation in Ho-sublattice.

3.3 Neutron powder diffraction data

Figure. 4a shows observed and calculated NPD patterns of $Ho(Fe_{0.12}Co_{0.88})_2$ at 293 K. All set of reflections, originated from $Ho(Co_{0.88}\ Fe_{0.12})_2$ crystal structure, are observed on NPD patterns and there are not additional peaks. So, it additionally confirms that we deal with a good single phase sample. Calculation of reflection's intensities results that Ho-ions occupy the 8*a* position and

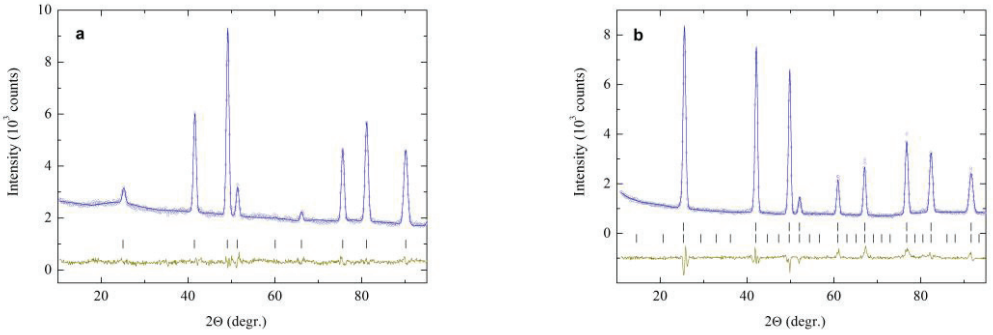

Figure. 4: Neutron powder diffraction patterns of $Ho(Fe_{0.12}Co_{0.88})_2$ at 293 K (**a**) and 78 K (**b**)

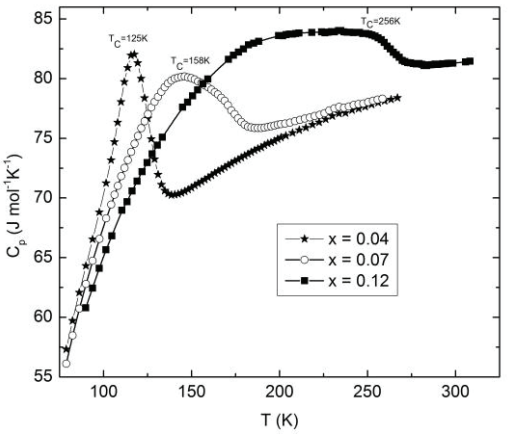

Figure. 5: Heat capacity temperature dependencies – Cp(T) for $Ho(Co_{1-x}Fe_x)_2$ compounds

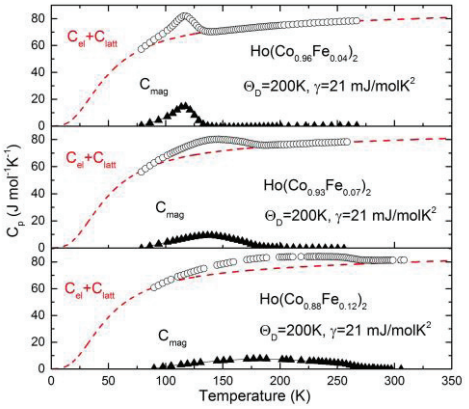

Figure. 6: Heat capacity temperature dependencies for $Ho(Co_{1-x}Fe_x)_2$ compounds. Experimental data – open symbols, calculated lattice and electronic contributions ($C_{el} + C_{latt}$) – dashed line, magnetic contribution (C_{mag}) – closed symbols

Co/Fe-atoms are located at the 16*d* sites. The best agreement (Global Chi^2 = 3.2 %) between experimental and calculated intensities is reached if the refinement composition of the sample as $Ho(Co_{0.91}Fe_{0.09})_2$ is considered.

Figure. 4b presents observed and calculated NPD patterns of $Ho(Co_{0.88}Fe_{0.12})_2$ at 78 K. Comparing Figure. 4a and 4b data point it can a strong magnetic contribution existence in many reflections, especially to first reflection. Refinement (Global Chi^2 = 3.8 %) of crystal and magnetic structure parameters results that a magnetic order in $Ho(Co_{0.88}\ Fe_{0.12})_2$ is described by the propagation vector $\boldsymbol{k} = 0$. Magnetizations of Ho-ions and Co/Fe-atoms are coupled antiferromagnetically. The magnetic moment of Ho-ions μ_{Ho} equals to 6.8(1) μ_B and that of Co/Fe-atoms $\mu_{Co/Fe}$ is 1.09 μ_B. Though this measurements have been performed at 78 K, we can assume that values of μ_{Ho} and $\mu_{Co/Fe}$ would be close to those at 5 K because the magnetization falls slowly over temperature region (5÷78 K) due to strong T_C increasing by a Co substitution with Fe. From comparing our results with data for $HoCo_2$ in (Moon., et al., 1965) we obtain that the value of the $\mu_{Co/Fe}$ is almost the same (μ_{Co} = 1.0(2) μ_B in (Moon., et al., 1965)) whereas a value of the μ_{Ho} decreased on 2.7 μ_B. According to (Moreau, et al., 1971) in $HoFe_2$ the value of the μ_{Ho} is equaled to 9.5(2) μ_B as in $HoCo_2$. Thus, we can conclude that Fe introduction induces the disorientation effect in Ho-ions magnetic ordering. An average inclination of Ho magnetic moments from Ho-Fe couple direction – [100] axis is equaled to 44 degrees.

3.4 Heat capacity

Temperature dependences of a heat capacity ($C_P(T)$) for $Ho(Co_{1-x}Fe_x)_2$ compounds are given in Figure. 5 (x = 0.04, 0.07, 0.12). For compound with minimal Fe-content (x=0.04) a rather narrow maximum of Cp(T) in the vicinity of Curie temperature is observed. Under the Fe-concentration increase its width is broadened. So it testifies the evident structural changes in substituted compounds. The total compound heat capacity (C) can be considered as a sum of third contributions – magnetic (C_{mag}), lattice (C_{latt}) and electronic (C_{el}) (Cwik, et al., 2013):

$$C = C_{mag} + C_{latt} + C_{el} = C_{mag} + 9Nk\left(\frac{T}{\theta_D}\right)^3 \int_0^{\frac{\theta_D}{T}} \frac{x^4 e^x}{(e^x-1)^2}\,dx + \gamma T, \quad (3)$$

where N – atoms number per formulae unit, R – universal gas constant (R = 8.314 J/molK), θ_D – Debay temperature, γ – electronic capacity coefficient.

Selection of γ and θ_D parameters was made for a definition of nonmagnetic contributions – C_{latt} and C_{el} using the experimental $C_P(T)$ curves for the higher Curie temperature range. It was found that for all studied compounds their magnitudes are very similar and have the following values: θ_D = 200 K and γ = 21 mJmol^{-1}K^{-2}. These data are also relatively close to that in RCo_2 paramagnetic compounds which have the same crystal structure as $Ho(Co_{1-x}Fe_x)_2$ intermetallics (Ikeda, et al., 1984): for YCo_2 γ = 35 mJmol^{-1}K^{-2} and θ_D = 222 K; for $LuCo_2$ γ = 32 mJmol^{-1}K^{-2} и θ_D = 238 K.

In Figure. 6 the electron-lattice (C_{el} + C_{latt}) and magnetic (C_{mag}) contributions temperature dependences are presented. As it seen, the magnetic contribution to a total heat capacity is observed in all compounds and its existence propagates to more wider temperature range upon the Fe content rise but the absolute value of $C_m(T)$ maximum is decreased. It can be connected with the existence of magnetic order in Ho-sublattice up to the higher temperatures due to the increasing of T_c value giving a Ho-(Co,Fe) exchange interaction energy increase.

3.5 Magnetocaloric effect

For the calculation of isothermal entropy change (ΔS), which can be made using formulae (4) (Halder, et al., 2010; Gschneidner Jr. & Pecharsky, 2000), the samples magnetization field dependencies in the external

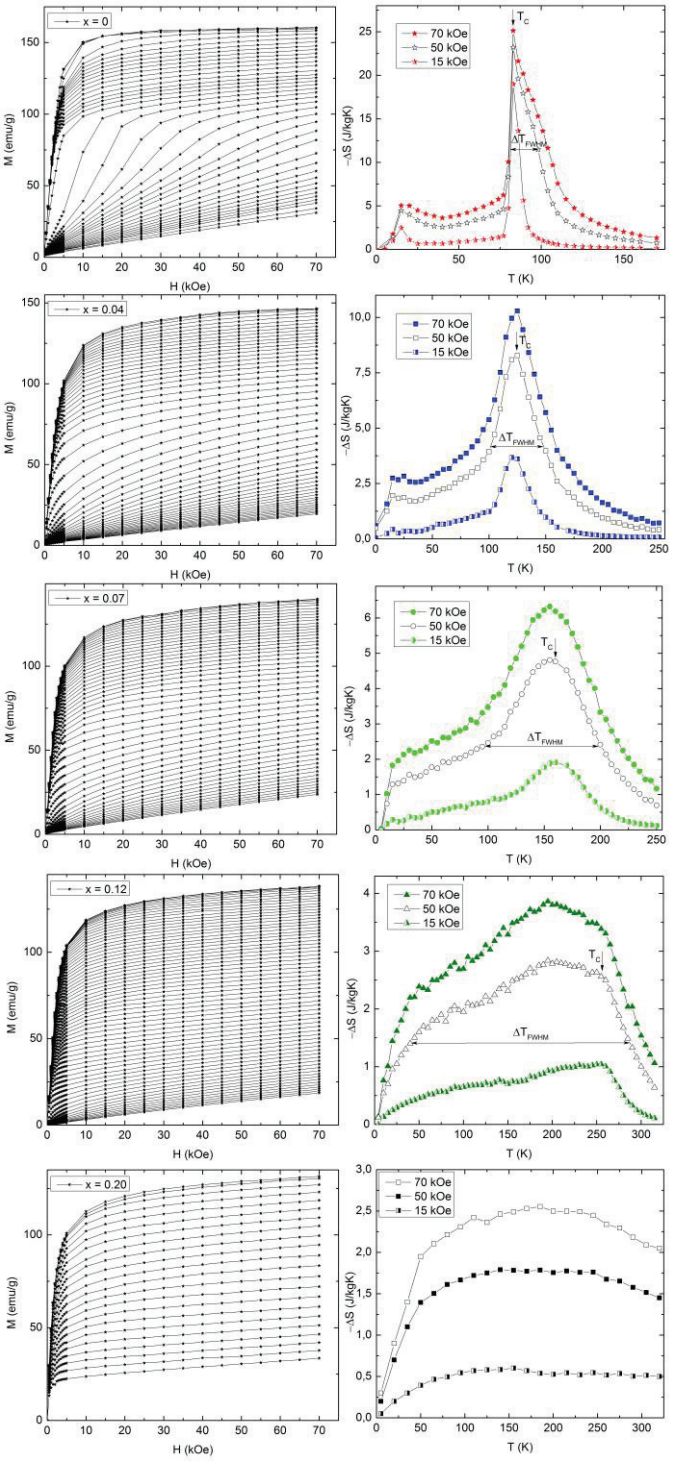

Figure. 7: Magnetization isotherms at various temperatures and magnetic entropy change temperature dependences -ΔS(T) for $Ho(Co_{1-x}Fe_x)_2$ in different magnetic fields

magnetic fields H = (0÷70) kOe in the wide temperature range with a step of 3÷15 K were performed (Figure. 7).

$$\Delta S(H,T) = \sum_i \frac{M_{i+1}(T_{i+1},H) - M_i(T_i,H)}{T_{i+1} - T_i} \Delta H. \quad (4)$$

Figure. 7 shows the calculated values of -ΔS data for the change of magnetic field $\Delta\mu_0 H$ = 70, 50 and 15 kOe. The figure shows that with iron concentration increasing, the ΔT_{FWHM} value, characterizing the difference between higher and lower temperatures at half maximum of the -ΔS(T) peak, increases. Similar trend of ΔT_{FWHM} increasing with magnetic field is observed for all $Ho(Co_{1-x}Fe_x)_2$ samples. Availability of ferromagnets with MCE in the wide temperature range is essential for its potential use in magnetic refrigerants.

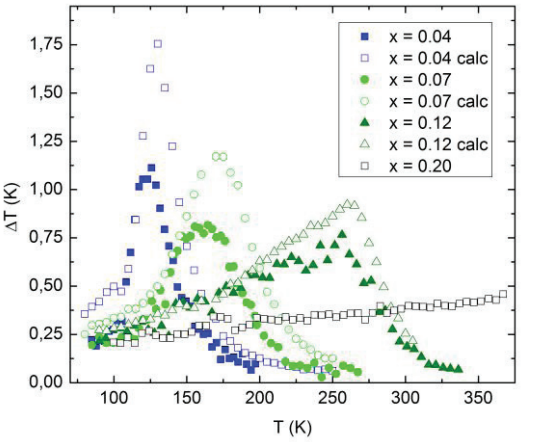

Figure. 8: Experimental and calculated using (4) MCE temperature dependencies (ΔT- effect) in $Ho(Co_{1-x}Fe_x)_2$ compounds

From Figure. 7 it follows that magnetic contributions to entropy of samples with x = 0 and 0.04 in all studied temperature range are positive, having characteristic maximum near T_C. The MCE temperature dependences of the samples with x = 0.07, 0.12 and 0.20 have more complicated character exhibiting the expressed plateau at $T < T_c$.

Such type of ΔS(T) dependence at low temperatures can be explained by the umbrella-like (canting) structure of Ho magnetic sublattice caused by the statistical non-uniform distribution of Fe-atoms around the rare-earth site. Therefore, in $Ho(Co_{1-x}Fe_x)_2$ compounds with x = 0.07, 0.12 и 0.20 MCE in the low temperature region originates from the Ho- magnetic sublattice structure and its transformation under an external magnetic field action. As it follows from this, when an external field is applied there will be a large paraprocess, and, therefore, the MCE as derivative $\partial M/\partial T$ will be great. Thus, in $Ho(Co_{1-x}Fe_x)_2$, at x = 0.07, 0.12 and 0.20 in the low temperatures region the MCE is almost completely defined by magnetic structure of a rare-earth sublattice and its change under magnetizing.

Figure. 8 shows the temperature dependence of the magnetocaloric effect in $Ho(Co_{1-x}Fe_x)_2$ compounds determined by direct ΔT-measurements in magnetic field of 17 kOe, as well as the calculated one from M(H) data on the magnetic field change ΔH = 15 kOe. For MCE calculation for (ΔT_{calc}) values, the following formulae were used (Gschneidner Jr. & Pecharsky, 2000):

$$\Delta T_{calc}(T) = - \frac{T}{C_{P,H}(T)} \Delta S_H(T) \quad (4)$$

where $C_{P,H}$ is the heat capacity of the sample material at the DC magnetic field, ΔS_H is the change of magnetic entropy part. Because of the absence of data on the temperature dependences of heat capacity for the DC magnetic field of 15 kOe, the calculation of ΔT_{calc} was performed using the value of $C_{P,H}$ under H = 0 (Figure. 5). It can be concluded that ΔT_{calc} peak shape and its values are close to those obtained by direct measurements. Differences between calculated and measured ΔT-effect values can be connected with the using of zero field C_P data and possible non included contributions to (4). The same divergences of the measured and calculated ΔT-effect data was found in case $HoCo_2$ for the magnetic field of 20 kOe (6 K and 3.2 K recpectively) (Sechovsky, et al., 2007; Nikitin & Tishin, 1991).

We calculated also the refrigerant (cooling) capacity (q), using the following formula (Gschneidner Jr. & Pecharsky, 2000):

$$q = -\int_{T_1}^{T_2} \Delta S dT, \quad (5)$$

where T_1 and T_2 are the lowest and the highest temperatures on the T-axis, corresponding to half-height maximum of ΔS(T) dependence. The refrigerant capacity determines the efficiency

of a magnetocaloric material. For the sample with x = 0.12 it was found to be 583 J/kg (H = 50 kOe), that is almost twice higher than that of 299 J/kg for $Tb(Co_{0.7}Fe_{0.3})_2$ with close T_c value (Halder, et al., 2010) and 15% higher the q-value for $Dy(Co_{0.90}Fe_{0.10})_2$,compound studied by us in paper (Anikin, et al., 2015b).

Conclusion

Summarizing, we can conclude that the magnetocaloric effect in iron substituted $Ho(Co_{1-x}Fe_x)_2$ type compounds has also untypical behavior as in similar $R(Co_{1-x}Fe_x)_2$ intermetallics. The common feature of this phenomenon is the manifestation of significant magnetic entropy change in the temperature range below of their magnetic ordering temperature. Such magneto-thermal property behavior of these magnetic materials is very useful and interesting both from practical and scientific points of view. Apparently, the partial replacement of Co-ions with relatively low atomic magnetic moments on Fe-ion, leads to formation of sperimagnetic structure in substituted compounds (Ho-ions magnetic moments orientations randomization) at low temperatures. Fe-ions as it was shown earlier (Deryagin, et al., 1979), usually have the higher effective electric charge in $R_m(Co,Fe)_n$ type intermetallics which can strongly change the local crystal electric field acting on the R-ion 4f electronic shell and deflects the R-ion magnetic moment orientation from the global easy axis.

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