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Magnetic and magnetocaloric properties of $\text{Gd}_6(\text{Mn}_{1-x}\text{Co}_x)_{23}$ compounds ($x \leq 0.3$)

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Abstract.

The magnetic and magnetocaloric properties of the $\text{Th}_6\text{Mn}_{23}$ -type structure $\text{Gd}_6(\text{Mn}_{1-x}\text{Co}_x)_{23}$ ($x \leq 0.3$) compounds are investigated from DC magnetization measurements. The Curie temperature of these ferrimagnetic materials evolves non-continuously with the Co content from $T_C = 489$ K for $x = 0$ to $T_C = 118$ K for $x = 0.3$. In relation with the lower magnetic moment of Co atoms compared with that of Mn atoms, the Co to Mn substitution leads to a decrease of the maximal magnetization, recorded at 5 K in an applied magnetic field of 9 T, from $54.7 \mu_B/\text{f.u.}$ for $x = 0$ to $36.3 \mu_B/\text{f.u.}$ for $x = 0.3$. These materials present an anomalous magnetocaloric effect, characterized by two broad $-\Delta S_M$ maxima of moderate magnitude at T_C and around 100 K, yielding to wide magnetocaloric response from T_C down to the lowest temperature, and consequently, a relatively large cooling capacity $q_{10-350\text{K}}$ ($\mu_0\Delta H = 5$ T) reaching $\sim 3.7 \text{ J}\cdot\text{cm}^{-3}$ for $\text{Gd}_6(\text{Mn}_{0.875}\text{Co}_{0.125})_{23}$. The results are analyzed and discussed in connection with previously published data.

Keywords: Lanthanide intermetallic compound, Magnetic properties, Magnetocaloric properties, Magnetic entropy change

1. Introduction

Research activity for identifying new magnetic materials having magnetocaloric properties suited to potential magnetic refrigeration applications near or below room temperature [1-4] is of increasing interest since the discovery of the giant magnetocaloric effect [5,6]. Part of the present research activity on magnetocaloric effect (MCE) applications is devoted to gas liquefaction technology, especially in view of storage and transportation of emerging fuels (e.g. hydrogen, natural gas) [7,8]. Magnetocaloric liquefaction is expected to be more efficient and more ecological than conventional gas-cycle liquefiers. For practical applications materials should display a large magnetocaloric effect (MCE) extending over a significant temperature interval. Moreover, it should be made from cheap, abundant, and non-toxic elements and should be easy to fabricate and to machine [2,9].

In previous papers, we investigated the magnetocaloric properties of the $\text{Th}_6\text{Mn}_{23}$ -type R_6Mn_{23} compounds (R = a rare-earth) [10] and some of their derivatives, namely $\text{Gd}_{6-x}\text{R}_x\text{Mn}_{23}$ [11] and $\text{Gd}_6(\text{Mn}_{1-x}\text{Fe}_x)_{23}$ [12]. In these ferrimagnetic materials, the R and T (= Mn or Fe)

sublattices order magnetically at two different temperatures which can be altered by chemical substitutions. The Mn sublattice orders above 400 K [10]. Fe substitution allows reducing the ordering temperature down to ~ 100 K in $\text{Gd}_6(\text{Mn}_{1-x}\text{Fe}_x)_{23}$ with x varying from 0.3 to 0.5 [12,13]. The maximum R ordering temperature is as expected observed for $R = \text{Gd}$ [10], which has the highest de Gennes factor among the 4f elements, near ~ 100 K. Substituting Gd with another heavy rare-earth element allows displacing the R ordering to lower temperatures [11]. This yields a partially tunable magnetocaloric response of moderate magnitude ($< 45 \text{ mJ.cm}^{-3}.\text{K}^{-1}$ for $\mu_0\Delta H = 5 \text{ T}$) but which extend over a broad temperature interval, providing thus a relatively high cooling capacity between 10 K and 350 K (for $\mu_0\Delta H = 5 \text{ T}$) which reaches $q = 4.2 \text{ J.cm}^{-3}$ for $\text{Ho}_6\text{Mn}_{23}$ [10].

Due to their complex crystal and magnetic structures, the $R_6\text{Mn}_{23}$ compounds involving a heavy rare-earth R element have the features to possess a higher magnetization than those involving light rare-earth element [10]. The $R_6\text{Mn}_{23}$ ($R = \text{Y, Nd, Sm, Gd-Tm, Lu}$) compounds crystallize in the $\text{Th}_6\text{Mn}_{23}$ -type structure (space group $Fm-3m$), which comprises one crystallographic site for the R atoms and four sites for the Mn atoms (4b, 24d, 32f₁, and 32f₂) [10,14,15]. From polarized neutron diffraction experiments on Y_6Mn_{23} a collinear ferrimagnetic arrangement has been found due to the antiparallel alignment of the 32f₁ and 32f₂ magnetic moments with those of the 4b and 24d sites [16]. The refined Mn moments values at 4.2 K are: ~ -2.8 , ~ -2.1 , $\sim +1.8$, and $\sim +1.8 \mu_B$ on the 4b, 24d, 32f₁, and 32f₂ sites, respectively [16]. Hence, the net magnetization is parallel to the 32f₁ and 32f₂ sites magnetic moments. In $R_6\text{Mn}_{23}$ compounds involving a heavy rare-earth element, the R magnetic moments couple antiferromagnetically with the less magnetized of the Mn sublattices to form complex non-collinear magnetic structures [16,17]. The (usual) negative sign of the Gd-Mn magnetic exchange has been confirmed by neutron inelastic scattering on $\text{Gd}_6\text{Mn}_{23}$ [18]. The decrease of both the magnetization and the ordering temperature upon Fe substitution in $\text{Gd}_6(\text{Mn}_{1-x}\text{Fe}_x)_{23}$ is due to the Fe atoms carrying a lower magnetic moment than the Mn atoms in these phases [12].

In this paper, we focus on the $\text{Gd}_6(\text{Mn}_{1-x}\text{Co}_x)_{23}$ (with $x \leq 0.3$) solid solution with the aim to determine the magnetic and magnetocaloric properties of these compounds and to explore their potential interest for future cooling applications as active and/or passive materials.

2. Experimental details

The $\text{Gd}_6(\text{Mn}_{1-x}\text{Co}_x)_{23}$ compounds with $x = 0, 0.01, 0.03, 0.07, 0.1, 0.125, 0.15, 0.2, 0.3$ and 0.4 have been synthesized starting from stoichiometric amounts of high-purity elements (Gd 99.9 wt.% from Rhodia, Mn 99.99 wt.% from Cerac and Co 99.8 wt.% from Cerac). The mixtures were melted in a water-cooled copper crucible using a high frequency induction furnace (CELES) under pure argon atmosphere. The samples were not annealed after melting. The purity and chemical composition of each sample have been checked by microprobe analysis (Cameca SX 100) on mirror polished powder samples dispersed in a cold resin. Polishing was performed using SiC paper from 800 to 1200 grit under water, and finished with a $1\mu\text{m}$ diamond paste. The purity was evaluated from backscattered electron (BSE) micrographs on different particles and the chemical composition was determined from an average of six pinpoints randomly chosen among the sample. The crystallographic structure and the presence of impurities have been verified by powder X-ray diffraction (Philips X'Pert

Pro Diffractometer, Cu K α). The analysis of the patterns was performed by Rietveld profile refinement using the Fullprof and WinPlotr softwares [19,20].

The high temperature (from 300 K to 600 K) magnetic measurements were carried out using a MANICS DSM8 magnetosusceptometer in an applied magnetic field of 0.05 T. The low temperature (from 5 K to 350 K) field-cooled (FC) measurements were performed using a PPMS apparatus (Quantum Design) in an applied magnetic field of 0.05 T. This device was also used to perform magnetization measurements at 5 K (in fields up to 9 T) and to determine the magnetocaloric properties. The magnetic entropy change ($-\Delta S_M$, given in units of $\text{mJ}\cdot\text{cm}^{-3}\text{K}^{-1}$ as suggested by Gschneidner Jr. *et al.* [2]) was evaluated using one of the Maxwell relations:

$$\Delta S_M(T)_{\Delta H} = \mu_0 \int_0^{H_f} \left(\frac{\partial M}{\partial T} \right)_H dH \quad (1)$$

The numerical integration of Eq. (1) was carried out using the method proposed by Pecharsky and Gschneidner Jr. [21], from magnetization isotherms recorded on heating from 10 K to 350 K in fields up to $\mu_0 H_f = 5$ T, with field steps of 0.2 T and temperature increments of 5 K.

3. Experimental results and interpretation

3.1. Crystallographic data

The analysis of the powder X-ray diffraction patterns, shown in Figure 1, indicates that $\text{Gd}_6(\text{Mn}_{1-x}\text{Co}_x)_{23}$ compounds (with $x \leq 0.4$) crystallize in the $\text{Th}_6\text{Mn}_{23}$ -type structure (space group $Fm\bar{3}m$) [14] and form a continuous solid solution. The samples are found to be single-phase except for the $x = 0.4$ alloy, which evidences low intensity supplementary diffraction peaks, corresponding to $\text{Gd}(\text{Mn}_{1-x}\text{Co}_x)_{12}$ and $\text{Gd}(\text{Mn}_{1-x}\text{Co}_x)_2$ phases (Figure 1). These secondary phases are confirmed on higher cobalt content samples. Rietveld refinement of the $\text{Gd}_6(\text{Mn}_{0.6}\text{Co}_{0.4})_{23}$ pattern indicates less than 4 wt.% of these secondary phases in the sample.

Microprobe measurements show that the samples are homogenous, despite lack of annealing, and point to a slight sub-stoichiometry of cobalt (< 2 wt.%) compared to the nominal as weighted compositions. However, this weak sub-stoichiometry is reasonable taking into account the measurement errors. Chemical analysis indicate a maximum Co to Mn substitution of 35(2) at.% in $\text{Gd}_6\text{Mn}_{23}$. It is well-known that the limit of solubility commonly decreases with temperature. Then, this experimental value must be considered as a maximum and should not be higher in annealed samples.

Thus, we can conclude that the solubility of cobalt in as-cast $\text{Gd}_6(\text{Mn}_{1-x}\text{Co}_x)_{23}$ is limited to $x_{\text{max}} \sim 0.35$ (+/- 0.02). Considering that secondary phases detected in the $x = 0.4$ alloy could evidence magnetic properties [22,23], magnetic and magnetocaloric properties of this sample are not taken into account in the study.

The cell parameters and the crystallographic densities of $\text{Gd}_6(\text{Mn}_{1-x}\text{Co}_x)_{23}$ compounds (with $x \leq 0.3$) are gathered in Table 1. As expected from the atomic radii and atomic weights of the involved elements, the Co to Mn substitution leads to a linear decrease of the cell parameter (Figure 2) and, consequently, to a linear increase of the density. Because of the close X-ray scattering lengths factors of Mn and Co, no attempt has been done to determine the distribution of Co atoms over the four possible transition metal crystallographic sites.

3.2. Magnetic properties

The thermal variation of the magnetization of the $\text{Gd}_6(\text{Mn}_{1-x}\text{Co}_x)_{23}$ compounds, shown in Figure 3, have a typical shape of ferrimagnetic materials. The Curie temperatures T_C depend in a non-linear manner on the Co content (inset of Figure 3), decreasing upon Co for Mn substitution from $T_C = 489$ K for $x = 0$ to $T_C = 118$ K for $x = 0.3$ (Table 2). These results indicate that the magnetic ordering temperature in these materials is mainly dominated by the exchange interactions between transition metals. The decrease of the magnetic ordering temperature with the cobalt content is similar to that observed in the manganese-rich part of the $\text{Gd}_6(\text{Mn}_{1-x}\text{Fe}_x)_{23}$ series [12,24-26]. However the Curie temperature, for the same atomic substitution value x , are lower for the $\text{Gd}_6(\text{Mn}_{1-x}\text{Co}_x)_{23}$ compounds than for the $\text{Gd}_6(\text{Mn}_{1-x}\text{Fe}_x)_{23}$ compounds [12,24-26].

The field dependence of the magnetization at 5 K recorded up to an applied magnetic field of 9 T is shown in Figure 4. Absence of magnetic hysteresis and weak metamagnetic-like transition observed for the lower Co content compounds ($x \leq 0.03$) confirm the ferrimagnetic behavior of these materials. Similarly to the Fe derivatives [12], the Co substitution leads to the disappearance of the metamagnetic-like transition observed near a threshold field of 5 T on the isotherm magnetization curve of the binary $\text{Gd}_6\text{Mn}_{23}$ compound. For the higher Co contents ($x > 0.1$), a weak magnetic hysteresis is observed at low magnetic field ($\mu_0 H < 1$ T), leading to a negligible remanent magnetization ($< 4 \mu_B/\text{f.u.}$), except for $x = 0.3$, where it reaches $12.7 \mu_B/\text{f.u.}$ (Figure 4).

The maximal magnetization depends in a comparable manner on the cobalt content than the magnetic ordering temperature: it decreases from $54.7 \mu_B/\text{f.u.}$ for $x = 0$ to $36.3 \mu_B/\text{f.u.}$ for $x = 0.3$ (Table 2). This non-linear variation of both the magnetic ordering temperature and maximal magnetization is very similar to that observed in the manganese-rich part of the $\text{Gd}_6(\text{Mn}_{1-x}\text{Fe}_x)_{23}$ solid solution [12,24-26], and thus, similar interpretation can be considered. The Co atoms carry a lower magnetic moment than the Mn atoms. Upon increasing the Co content, the Co atoms predominantly localize on the $32f_1$ site, as do the Fe atoms [27]. The $32f_1$ moments interact ferromagnetically with the Gd moments [16], leading to a reduction of the magnetization and of the exchange interactions, and thus, of the magnetic ordering temperature.

3.3. Magnetocaloric properties

The thermal variation of the magnetic entropy change ($-\Delta S_M$) has been recorded only for the higher Co content samples ($x \geq 0.1$). The $-\Delta S_M$ curves recorded between 10 K and 350 K for a field variation $\mu_0 \Delta H$ of 5 T, 3 T, and 1 T are shown in Figure 5, and are compared to that of the parent $\text{Gd}_6\text{Mn}_{23}$ compound [12]. Similarly to the $\text{Gd}_6(\text{Mn}_{1-x}\text{Fe}_x)_{23}$ solid solution [12], these materials are characterized by a low to moderate magnetocaloric effect in the whole magnetic ordered temperature range with two maxima near 100 K, corresponding to the magnetic ordering of the gadolinium sublattice [10], and at the magnetic ordering temperature T_C . The increase of the Co content induces a decrease of the Curie temperature T_C , and thus, a shift of the corresponding $-\Delta S_M$ peak to the low temperatures, leading to a merging of the two maxima for $0.15 \leq x \leq 0.3$ (Figure 5). As a consequence, the magnitude of the low temperature maximum and the maximum magnetic entropy change $-\Delta S_M^{\text{max}}$ are found to increase (Figure 5 and Table 2) despite the concomitant reduction of the magnetization (Table 2).

The so-called cooling capacity $q = \int_{T_1}^{T_2} -\Delta S_M(T) dT$ gives an estimate of how much heat can be transferred between the cold (T_1) and hot (T_2) sinks in one ideal refrigeration cycle [2]. From the q values gathered in Table 2, we conclude that the refrigerant capacity of $\text{Gd}_6(\text{Mn}_{1-x}\text{Co}_x)_{23}$ materials between 10 K and 350 K (for a field variation of 5 T) is increased with the Co content from 2856 mJ.cm^{-3} for $x = 0$ to 3677 mJ.cm^{-3} for $x = 0.125$, due to the concentration at low temperatures of the magnetocaloric effect associated with the transition metal sublattices magnetic orderings. Finally, the refrigerant capacity $q_{10-350\text{K}}$ decreases continuously from $x = 0.125$ to $x = 0.3$ (Table 2). This reduction can be attributed to the lower magnetic moment of Co atoms compared to Mn atoms. The very large $q_{10-350\text{K}}$ values of these materials are comparable with those of the $\text{Gd}_6(\text{Mn}_{1-x}\text{Fe}_x)_{23}$ compounds [12] and with those of the best near room temperature magnetocaloric materials which are however calculated over a smaller temperature interval of 50 K around their T_C [2].

4. Summary and conclusion

In this study, we have investigated the magnetic and magnetocaloric properties of $\text{Gd}_6(\text{Mn}_{1-x}\text{Co}_x)_{23}$ ($x \leq 0.3$) compounds. Both the magnetic ordering temperatures and the magnetizations reduce upon increasing the Co content. This is related to the lower magnetic moment of Co atoms than that of the Mn atoms for one hand, and preferred crystallographic sites occupation of Co atoms to another hand. These compounds display an anomalous magnetocaloric response of moderate amplitude but covering a broad temperature range extending from their T_C down to low temperature. In most cases, two maxima can be distinguished related to the magnetic ordering of the transition metal (T_C) and gadolinium (around 100 K) sublattices. Due to the concentration of the magnetocaloric effect to the lower temperature, the cooling capacity $q_{10-350\text{K}}$ is then increased upon increasing the Co content, indicating that a partial cobalt to manganese substitution is beneficial for a magnetocaloric effect point of view. A maximum value of 3677 mJ.cm^{-3} is measured for $x = 0.125$. These materials have similar magnetic and magnetocaloric properties than those reported in the manganese-rich part $\text{Gd}_6(\text{Mn}_{1-x}\text{Fe}_x)_{23}$ series [12]. However, considering that cobalt is more expensive than iron, the applicative interest of $\text{Gd}_6(\text{Mn}_{1-x}\text{Co}_x)_{23}$ materials is then limited.

The R_6Mn_{23} phases and their derivatives may present some interests for magnetocaloric gas liquefaction technology despite their moderate MCE magnitude which is about 10 times lower than the peak value of the giant MCE materials [1-6]. By opposition with the latter, the MCE cover a broad temperature range in R_6Mn_{23} and their derivatives and since only second order transitions are involved, they are not penalized by the detrimental effects (hysteresis, slow kinetic, ageing) associated with first order transitions at the origin of the giant MCE. In 6-23 alloys, the temperature extent as well as the shape of the magnetocaloric response can be tuned through suited chemical substitutions on both the R and Mn sublattices. In particular, it is possible to target a 'plateau-like' magnetocaloric response as required by some ideal refrigeration cycles [28]. Another advantage of the 6-23 phases is that they are easy to fabricate, chemically stable and made from non-toxic elements.

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References

- [1] V.K. Pecharsky, K.A. Gschneidner Jr., *Magnetocaloric effect and magnetic refrigeration*, J. Magn. Magn. Mater. 200 (1999) 44-56.
- [2] K.A. Gschneidner Jr., V.K. Pecharsky, A.O. Tsokol, *Recent developments in magnetocaloric materials*, Rep. Progr. Phys. 68 (2005) 1479.
- [3] E. Brück, *Developments in magnetocaloric refrigeration*, J. Phys. D: Appl. Phys. 38 (2005) R381-R391.
- [4] K.A. Gschneidner Jr., V.K. Pecharsky, *Thirty years of near room temperature magnetic cooling: Where we are today and future prospects*, Int. J. Refrig. 31 (2008) 945-961.
- [5] V.K. Pecharsky, K.A. Gschneidner Jr., *Giant magnetocaloric effect in $Gd_5(Si_2Ge_2)$* , Phys. Rev. Lett. 78 (1997) 4494-4497.
- [6] V.K. Pecharsky, K.A. Gschneidner Jr., *Tunable magnetic regenerator alloys with a giant magnetocaloric effect for magnetic refrigeration from ~20 to ~290 K*, Appl. Phys. Lett. 70 (1997) 3299-3301.
- [7] J. Barclay, K. Oseen-Senda, M. Skrzypkowski, *Unique features of liquefaction of hydrogen and natural gas using magnetic refrigeration*, 6th IIF-IIR International Conference on Magnetic Refrigeration, Victoria, Canada, 2014.
- [8] T. Numazawa, K. Kamiya, T. Utaki, K. Matsumoto, *Magnetic refrigerator for hydrogen liquefaction*, Cryogenics 62 (2014) 185-192.
- [9] V.K. Pecharsky, K.A. Gschneidner Jr., Ya. Mudryk, D. Paudyal, *Making the most of the magnetic and lattice entropy changes*, J. Magn. Magn. Mater. 321 (2009) 3541-3547.
- [10] P. Lemoine, A. Vernière, T. Mazet, B. Malaman, *Magnetic and magnetocaloric properties of R_6Mn_{23} ($R = Y, Nd, Sm, Gd-Tm, Lu$) compounds*, J. Magn. Magn. Mater. 323 (2011) 2690-2695.
- [11] P. Lemoine, A. Vernière, T. Mazet, B. Malaman, *Magnetic and magnetocaloric properties of $Gd_{6-x}R_xMn_{23}$ ($R = Y, Sm, Tb, Dy, Ho, and Er$) compounds*, J. Alloys Compd. 578 (2013) 413-418.
- [12] P. Lemoine, A. Vernière, T. Mazet, B. Malaman, *Magnetocaloric properties of $Gd_6(Mn_{1-x}Fe_x)_{23}$ alloys ($x \leq 0.2$)*, Solid State Commun. 150 (2010) 1556-1559.
- [13] H. Nagay, N. Oyama, Y. Ikami, H. Yoshie, A. Tsujimura, *The magnetic properties of pseudo-binary compounds, $Gd(Fe_{1-x}Mn_x)_2$ and $Gd_6(Fe_{1-y}Mn_y)_{23}$* , J. Phys. Soc. Jpn. 55 (1986) 177-183.
- [14] J.V. Florio, R.E. Rundle, A.I. Snow, *Compounds of thorium with transition metals. I. The thorium-manganese system*, Acta Cryst. 5 (1952) 449.
- [15] F.E. Wang, J.V. Gilfrich, D.W. Ernst, W.M. Hubbard, *Report on the crystal structure of Gd_6Mn_{23}* , Acta Cryst. 17 (1964) 931-932.
- [16] A. Delapalme, J. Déportes, R. Lemaire, K. Hardman, W.J. James, *Magnetic interactions in R_6Mn_{23} rare-earth intermetallics*, J. Appl. Phys. 50 (1979) 1987-1989.

- [17] B. Ouladdiaf, J. Deportes, J. Rodriguez-Carvajal, *Magnetic structures of Er_6Mn_{23} and Dy_6Mn_{23}* , Physica B 213 & 214 (1995) 330-332.
- [18] P. Tils, M. Loewenhaupt, K.H.J. Buschow, R.S. Eccleston, *Intersublattice exchange coupling in Gd-Mn compounds studied by INS*, J. Alloys Compd. 279 (1998) 123-126.
- [19] J. Rodriguez-Carvajal, *Recent advances in magnetic structure determination by neutron powder diffraction*, Physica B 192 (1993) 55-69.
- [20] T. Roisnel, J. Rodriguez-Carvajal, *WinPLOTR: a Windows tool for powder diffraction pattern analysis*, Mater. Sci. Forum 378-381 (2001) 118-123.
- [21] V.K. Pecharsky, K.A. Gschneidner Jr., *Magnetocaloric effect from indirect measurements: Magnetization and heat capacity*, J. Appl. Phys. 86 (1999) 565-575.
- [22] Y. Makihara, H. Fujii, K. Hiraoka, H. Nagata, T. Hihara, *Magnetic phase transitions in the $Gd(Mn_{1-x}Co_x)_2$ system*, J. Magn. Magn. Mater. 96 (1991) 305-314.
- [23] Y.G. Wang, P. Lin, C. Chen, Q. Wang, N. Tang, F. Yang, *Structure and magnetic properties of $GdMn_{12-x}Co_x$ compounds*, J. Mater. Sci. Lett. 17 (1998) 493-495.
- [24] H.R. Kirchmayr, W. Steiner, *Magnetic order of the compounds series $RE_6(Mn_xFe_{1-x})_{23}$ ($RE = Y, Gd$)*, J. Phys. Colloq. 32 (1971) C1-665.
- [25] H. Nagai, N. Oyama, Y. Ikami, H. Yoshie, A. Tsujimura, *The magnetic properties of pseudo-binary compounds, $Gd(Fe_{1-x}Mn_x)_2$ and $Gd_6(Fe_{1-y}Mn_y)_{23}$* , J. Phys. Soc. Japan 55 (1986) 177.
- [26] H. Nagai, T. Yokoyama, S. Katsuyama, Y. Amako, H. Yoshie, K. Adachi, *The anomalous behaviour of the electrical resistivities of $Gd(Fe,Mn)_2$ and $Gd_6(Fe,Mn)_{23}$* , J. Magn. Magn. Mater. 177-181 (1998) 1131-1132.
- [27] W.J. James, K. Hardman, W. Yelon, B. Kebe, *Structural and magnetic properties of $Y_6(Fe_{1-x}Mn_x)_{23}$* , J. Phys. Colloq. 40 (1979) C5 206-208.
- [28] A.M. Tishin, Y.I. Spichkin, *The magnetocaloric effect and its applications*, Institute of Physics Publishing, Bristol, 2003.

Table 1: Cell parameters refined at room temperature and derived crystallographic densities of $\text{Gd}_6(\text{Mn}_{1-x}\text{Co}_x)_{23}$ compounds

Compound	a (Å)	V (Å ³)	M _{vol} (g.cm ⁻³)
$\text{Gd}_6(\text{Mn}_{0.99}\text{Co}_{0.01})_{23}$	12.524(1)	1964.4(3)	7.46
$\text{Gd}_6(\text{Mn}_{0.97}\text{Co}_{0.03})_{23}$	12.511(1)	1958.5(3)	7.49
$\text{Gd}_6(\text{Mn}_{0.93}\text{Co}_{0.07})_{23}$	12.485(1)	1946.1(3)	7.55
$\text{Gd}_6(\text{Mn}_{0.9}\text{Co}_{0.1})_{23}$	12.462(1)	1935.2(3)	7.61
$\text{Gd}_6(\text{Mn}_{0.875}\text{Co}_{0.125})_{23}$	12.443(1)	1926.6(3)	7.65
$\text{Gd}_6(\text{Mn}_{0.85}\text{Co}_{0.15})_{23}$	12.427(1)	1919.3(3)	7.68
$\text{Gd}_6(\text{Mn}_{0.8}\text{Co}_{0.2})_{23}$	12.396(1)	1904.6(3)	7.76
$\text{Gd}_6(\text{Mn}_{0.7}\text{Co}_{0.3})_{23}$	12.335(1)	1876.9(3)	7.91

Table 2: Curie temperature (T_C), magnetization at 5 K for an applied magnetic field of 9 T (M_{\max}), maximum of the magnetic entropy change ($-\Delta S_M^{\max}$) and cooling capacity between 10 K and 350 K for a field variation of 1 T, 3 T, and 5 T ($q_{10-350\text{ K}}$) of $\text{Gd}_6(\text{Mn}_{1-x}\text{Co}_x)_{23}$

Compounds	$T_C \pm 5$ (K)	M_{\max} ($\mu_B/\text{f.u.}$)	$-\Delta S_M^{\max}$ ($\text{mJ}\cdot\text{cm}^{-3}\cdot\text{K}^{-1}$)			$q_{10-350\text{ K}}$ ($\text{mJ}\cdot\text{cm}^{-3}$)		
			1T	3T	5T	1T	3T	5T
$\text{Gd}_6\text{Mn}_{23}$	489	54.7	1.6	7.0	12.5	379	1589	2856
$\text{Gd}_6(\text{Mn}_{0.99}\text{Co}_{0.01})_{23}$	479	54.3	-	-	-	-	-	-
$\text{Gd}_6(\text{Mn}_{0.97}\text{Co}_{0.03})_{23}$	447	51.8	-	-	-	-	-	-
$\text{Gd}_6(\text{Mn}_{0.93}\text{Co}_{0.07})_{23}$	383	48.5	-	-	-	-	-	-
$\text{Gd}_6(\text{Mn}_{0.9}\text{Co}_{0.1})_{23}$	314	46.5	2.5	8.7	15.0	624	2129	3595
$\text{Gd}_6(\text{Mn}_{0.875}\text{Co}_{0.125})_{23}$	265	44.5	2.4	8.6	14.7	589	2155	3677
$\text{Gd}_6(\text{Mn}_{0.85}\text{Co}_{0.15})_{23}$	219	43.5	2.9	9.1	15.3	558	2052	3528
$\text{Gd}_6(\text{Mn}_{0.8}\text{Co}_{0.2})_{23}$	156	40.2	4.4	12.4	19.8	558	1978	3410
$\text{Gd}_6(\text{Mn}_{0.7}\text{Co}_{0.3})_{23}$	118	36.3	5.3	14.9	23.4	517	1786	3081

Figure 1: X-ray powder diffraction patterns at room temperature of $\text{Gd}_6(\text{Mn}_{1-x}\text{Co}_x)_{23}$ ($x \leq 0.4$) represented in logarithmic ordinate scale

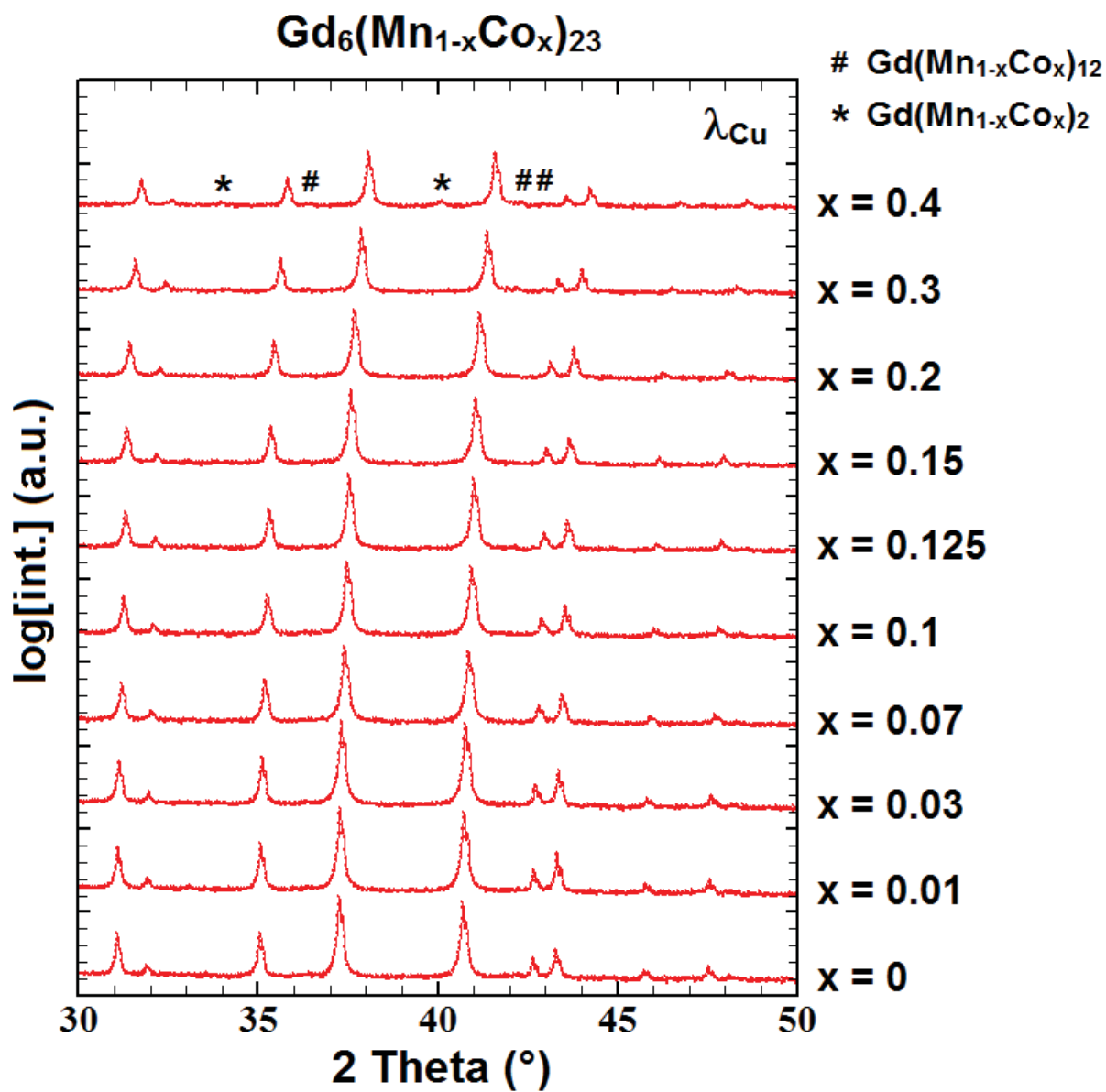


Figure 2: Variation of the cell parameter a with the value of the substitution parameter x in $\text{Gd}_6(\text{Mn}_{1-x}\text{Co}_x)_{23}$ solid solution (line is just a guide for eyes)

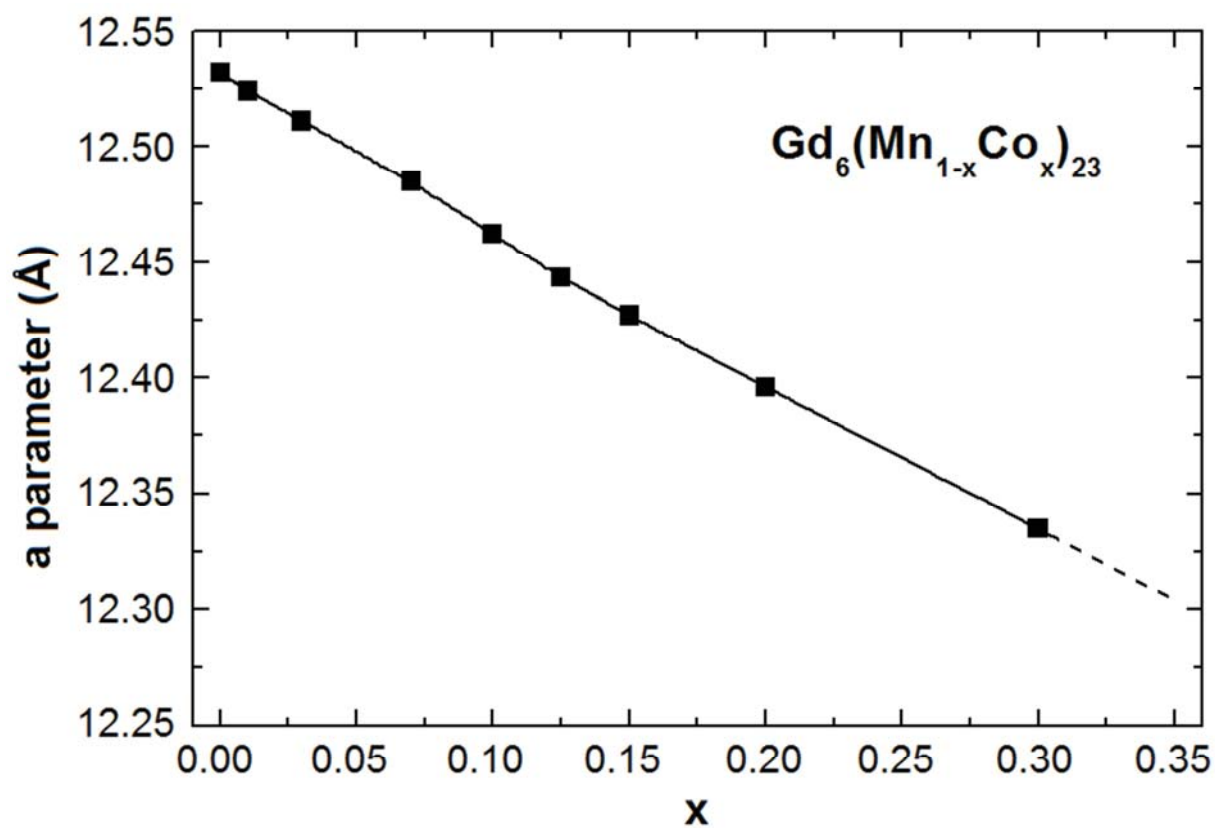


Figure 3: Thermal variation of the magnetization of $\text{Gd}_6(\text{Mn}_{1-x}\text{Co}_x)_{23}$ compounds in an applied magnetic field of 0.05 T. (Inset: variation of the Curie temperature (T_C) with Co content (line is just a guide for eyes))

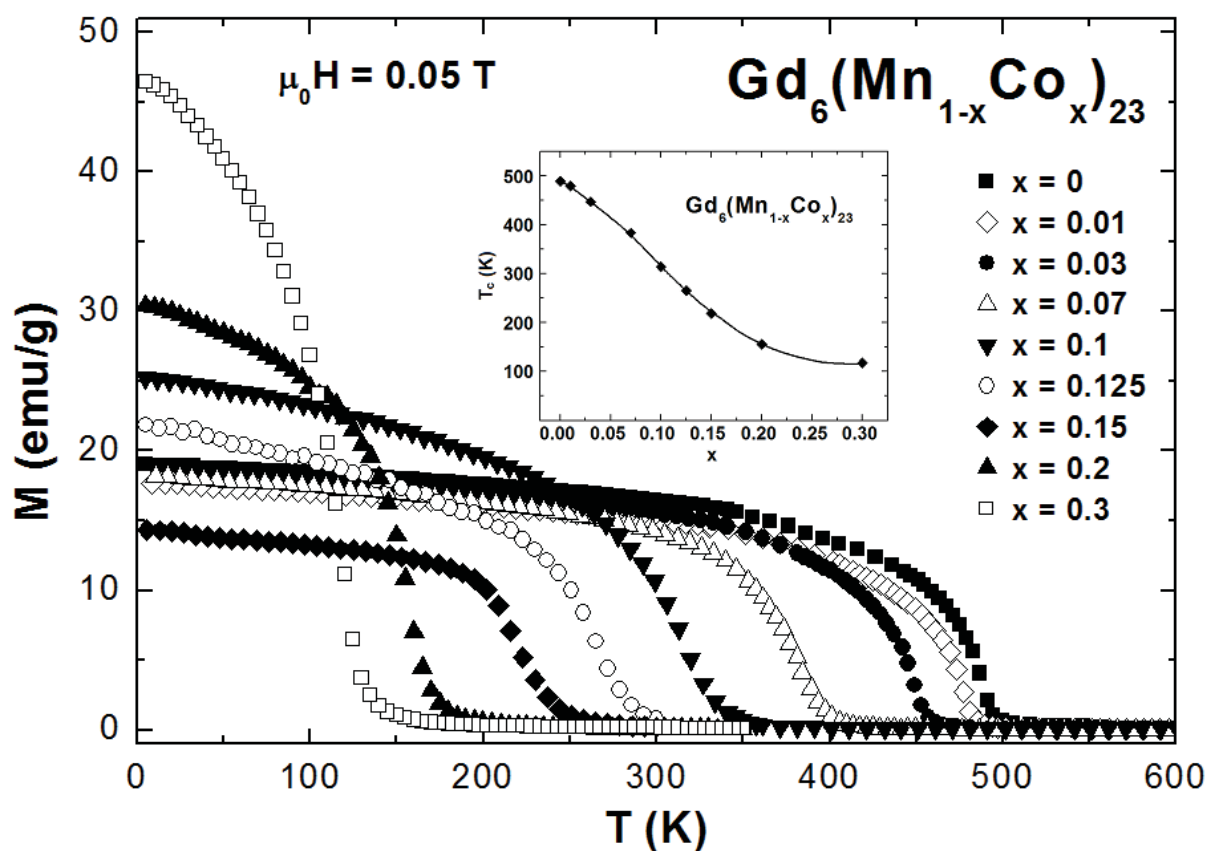


Figure 4: Field dependence of the magnetization of $\text{Gd}_6(\text{Mn}_{1-x}\text{Co}_x)_{23}$ compounds at 5 K in applied magnetic field up to 9 T

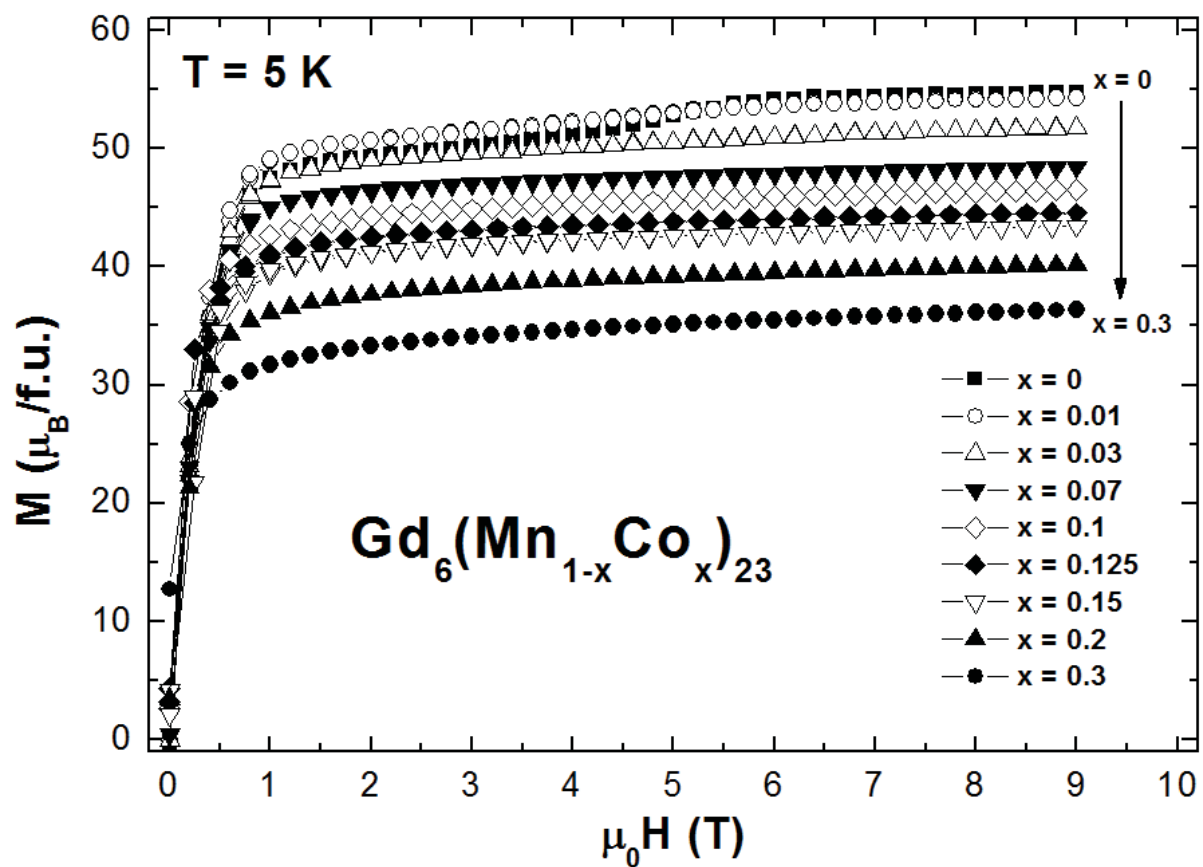
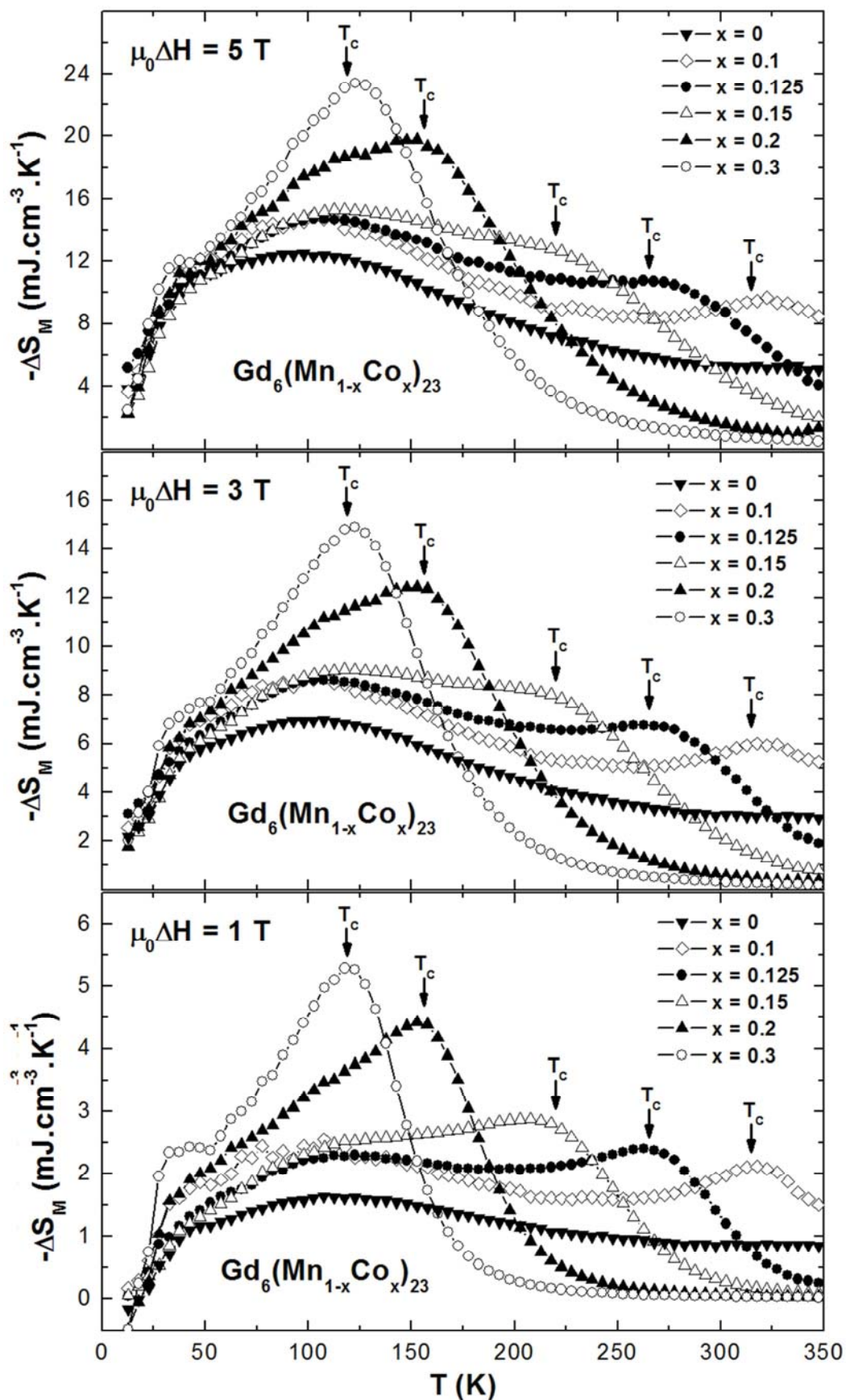


Figure 5: Temperature dependence of the magnetic entropy change in $\text{Gd}_6(\text{Mn}_{1-x}\text{Co}_x)_{23}$ compounds for a field variation of 5 T, 3 T, and 1 T



Highlights

- ✓ Determination of the limit of solubility of cobalt in the $\text{Gd}_6(\text{Mn}_{1-x}\text{Co}_x)_{23}$ solid solution
- ✓ Crystallographic data of $\text{Gd}_6(\text{Mn}_{1-x}\text{Co}_x)_{23}$ ($x \leq 0.3$) alloys from X-ray powder diffraction analyses
- ✓ Determination of the magnetic and magnetocaloric properties of the $\text{Gd}_6(\text{Mn}_{1-x}\text{Co}_x)_{23}$ ($x \leq 0.3$) compounds
- ✓ Concentration at low temperatures of the magnetocaloric effect associated with the transition metal sublattices magnetic orderings