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The Effect of Cr doping on the Magnetic and Magnetocaloric Properties of MnCoGe Alloys

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The structural, magnetic and magnetocaloric properties of $CoMn_{1-x}Cr_xGe$ (x=0.05-0.125) have been investigated by using electron microscopy, x-ray diffraction, calorimetric and magnetic measurements. In this study, our aim is to justify the magnetocaloric effect by tuning the structural and magnetic transition temperature with Cr doping on CoMnGe pure system. The substitution of Cr for Mn leads to a decrease of both structural and magnetic transition temperatures. However, structural and magnetic transition temperatures do not close to each other. From magnetization measurement, we calculate that isothermal entropy change associated with magnetic transition can be as high as 3.82 J $kg^{-1}K^{-1}$ at 302 K in a field of 7 T. Meanwhile, structural phase transition contribution to isothermal entropy change is calculated as 5.85 J $kg^{-1}K^{-1}$ at 322 K for 7 T.

Keywords : magnetic properties, magnetocaloric effect, arrott plots, phase transitions

1. Introduction

Caloric effects are inherent to every material. They refer to both adiabatic temperature change and isothermal entropy change that occurs when the external field is modified. Over the last decade, basic research on caloric effects has enjoyed enormous growth. Thus far, the most studied caloric effect is the magnetocaloric effect (MCE); and, after the discovery of the giant magnetocaloric effect in Gd-Si-Ge compounds, a variety of advanced magnetocaloric materials have been discovered [1]. Several authors have summarized the MCE and recent progress on it very well [2-5]. Magnetic refrigeration based on the MCE is an emerging technology for replacing current compression refrigeration because of its environmental friendliness and high efficiency [1-6].

Recently, lots of effort has been devoted to study of magnetocaloric effects associated with materials with first order magnetic phase transition rather than continuous magnetic phase transition near room temperature [7-12]. However, the presence of magnetic and thermal hysteresis-generic in practice to the dynamics of a first order phase transition-provides a potential obstacle to the use of first order magnetocaloric effects. Hysteresis limits the efficiency of the cycle by reducing the effective cooling power of the refrigerant.

CoMnGe shows first order magnetic transition and martensitic structural transformation from a low-temperature orthorhombic TiNiSi-type structure (space group Pnma) to a high-temperature hexagonal Ni_2In-type structure (space group $P6_3/mmc$). Several groups have investigated the CoMnGe [12-17]. It has been observed that the T_{struct} of this transition is highly dependent on the level of occupation of the Mn and Co sites [18]. Therefore, the T_{struct} of CoMnGe varies from 420 K to 650 K [18]. The magnetism of CoMnGe is based on localized Mn and Co moments, within in the ferromagnetic, orthorhombic ground state [19]. This state has a T_C of approximately 345 K [10]. Quenching the material from 1200 K can form a metastable hexagonal state, and this form of the material has a lower saturation moment as well as a lower T_C, roughly 283 K [14]. CoCrGe is a less studied material. Wirringa et al. showed that it has a $P6_3/mmc$ hexagonal structure and it is a ferromagnet. However, no Curie temperature was reported [20]. Although no transition to a low temperature orthorhombic phase was observed, $T_{struct} < T_{C\ is}$ as in Ref 18. Finally, $T_{struct} > T_C$ in CoMnGe, whereas $T_{struct} < T_C$ in CoCrGe. There is, consequently, the possibility that $CoMn_{1-x}Cr_xGe$ could exhibit a combined, magnetostructural transition if T_{struct} and T_C can be tuned together in

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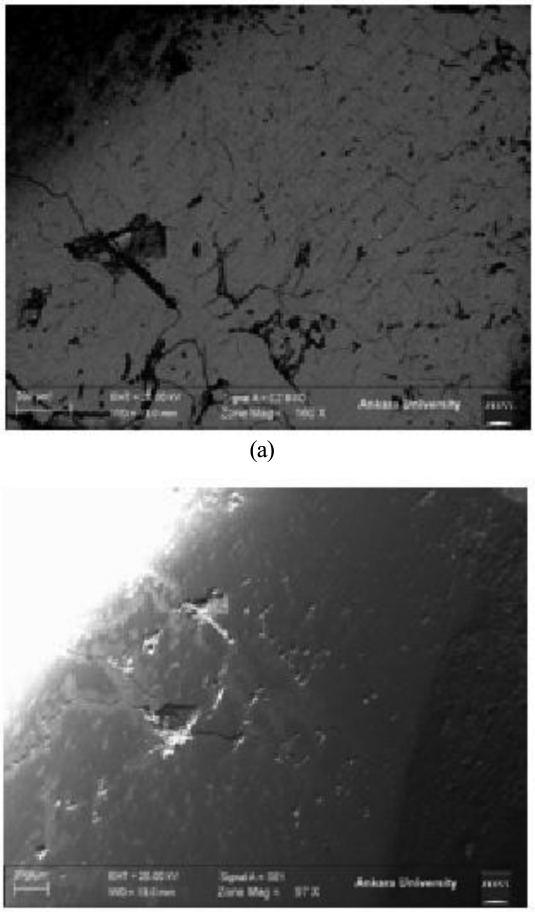
CoMnGe-based materials. Therefore, the motivation of this article is to present the influence of Cr substitution for Mn on the structural, magnetic and magnetocaloric properties of the new alloy system, $CoMn_{1-x}Cr_xGe$. We have analyzed the magnetocaloric effect of the material system, particularly in the region where a continuous Curie temperature and a first order martensitic structural phase transition are tuned together.

2. Experimental

The polycrystalline $CoMn_{1-x}Cr_xGe$ (x=0.05-0.125) alloys approximately 1 g were prepared by arc-melting appropriate amounts of the high purity constituent elements (Co 99.995%, Mn 99%, Fe 99.98% and Ge 99.9999%) under Ar atmosphere in a water-cooled copper crucible. In order to achieve high purity each element was arc-melted at least 3 times solely. Then, elements were arc-melted as a whole to achieve the alloy. The polycrystalline $CoMn_{1-x}Cr_xGe$ (x=0.05-0.125) was then encapsulated under an Ar atmosphere in quartz glass. In order to obtain a homogeneous phase, this encapsulated sample was annealed for four days at 1273 K and slowly cooled down to room temperature. The composition of the alloy was determined with energy dispersive X-ray analysis (EDX) by using the EVO 40 scanning electron microscope (SEM). Samples preparation, SEM-EDX (Zeiss EVO 40), powder X-ray diffraction measurements (Rigaku D-max 2200) and Magnetic (Quantum Design-PPMS) measurements were done in Ankara University. Differential scanning calorimetry (DSC) measurements were carried out using DSC Netzsch DSC 204 F1 with an empty aluminum pan as a reference in UNAM, Bilkent University. The DSC measurements were carried out during both the heating and cooling cycles with a scanning rate 10 K/min within the temperature range 325 K to 475 K. The magnetization measurements were made in a physical properties measurement system (PPMS) with a magnetic field up to 7 T within the temperature range 5 K to 350 K. Since the M (*T*) measurements in the different modes provide us more information about the magnetic properties of the alloys, the temperature dependence of magnetization was measured in zero-field-cooled (ZFC), field-cooled (FC) and field-heated (FH) modes.

3. Results and Discussion

Figure 1 shows back-scattered electron image of $CoMn_{0.875}Cr_{0.125}Ge$ after homogenization heat treatment. Since structural and magnetic properties highly dependent on the composition, we performed EDX analysis by using SEM for samples. EDX analysis revealed that alloys are uniform in composition. For instance, the average composition calculated from EDX analysis of the $CoMn_{0.875}Cr_{0.125}Ge$ sample, are found to be 32.85% for Co, 29.34% for Mn, 4.60% for Cr, and 33.21% for Ge. The reported compositions are an average of multiple points on the alloy, and no compositional heterogeneity was observed.



(a)

(b)

Fig. 1. (a) Back-scattered electron image and (b) SE image of $CoMn_{0.875}Cr_{0.125}Ge$ after homogenization heat treatment.

Figure 2 shows the DSC measurement of the $CoMn_{0.95}Cr_{0.05}Ge$. The difference between the peak temperatures of the heating and cooling curves indicated by the vertical dashed lines in Fig. 2 demonstrates the presence of a hysteresis associated with a first order structural phase transition. The martensitic transformation temperatures are shown in Fig. 2.

The width of the thermal hysteresis of the martensitic transformation of the $CoMn_{0.95}Cr_{0.05}Ge$ (the difference between T_{A-M} and T_{M-A}) is 45 K. The $CoMn_{0.875}Cr_{0.125}Ge$ and $CoMn_{0.9}Cr_{0.1}Ge$ shows similar behavior to the $CoMn_{0.95}Cr_{0.05}Ge$ sample (insets of Fig. 2). The width of the thermal hysteresis of $CoMn_{0.875}Cr_{0.125}Ge$ is 29 K. Table 2

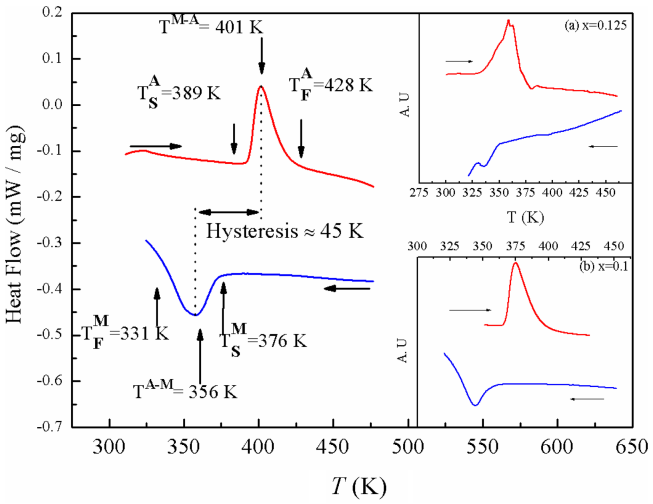


Fig. 2. (Color online) DSC measurement of the $CoMn_{0.95}Cr_{0.05}Ge$ alloy (inset (a) and (b) shows DSC measurement of $CoMn_{0.875}Cr_{0.125}Ge$ and $CoMn_{0.9}Cr_{0.1}Ge$ alloy, respectively).

shows the structural phase transitions of the $CoMn_{1-x}Cr_xGe$ (x=0, 0.05, 0.1, 0.125) alloys.

The martensitic transformation temperature of samples $CoMn_{1-x}Cr_xGe$ (x=0.05, 0.1 and 0.125) were found 401 K, 375 K and 358 K while magnetic transition temperatures were 322 K, 316 K and 308 K, respectively. Therefore, these alloys do not show forward transformation at room temperatures. Since there is no forward transition at room temperature, these alloys should have orthorhombic phase at room temperature. Consistent with DSC result, it was found that samples x=0.05, 0.1 and 0.125 have dominant orthorhombic phase from x-ray diffraction measurement. The difference between these two alloys is while sample x=0.05 has orthorhombic phase with two different unit cell parameters, sample x=0.125 has dominant orthorhombic phase besides negligible minor hexagonal phase (2.19%).

Figure 3(a), (b) & (c) shows Rietveld refinement of powder x-ray measurements of these alloys. In line with the DSC measurements, it was found dominant orthorhombic phase for x=0.05, 0.1 and x=0.125 samples. The unit cell parameters obtained from Rietveld refinements were given in Table 1.

Figure 4 shows temperature dependent magnetization of $CoMn_{1-x}Cr_xGe$ (x=0.05, 0.1 & 0.125) alloys within the temperature range of 5 K-350 K in a magnetic field of 0/01 T. The x=0.05, 0.1 & 0.125 alloys have ferromagnetic character below T_C values of 322 K, 316 K, 308 K, respectively, and are paramagnetic above this temperature. There is no thermal hysteresis between FC and FH curves in all alloys (in Fig. 4(a), (b) and (c)). This means that these alloys have no structural transition in this temperature range.

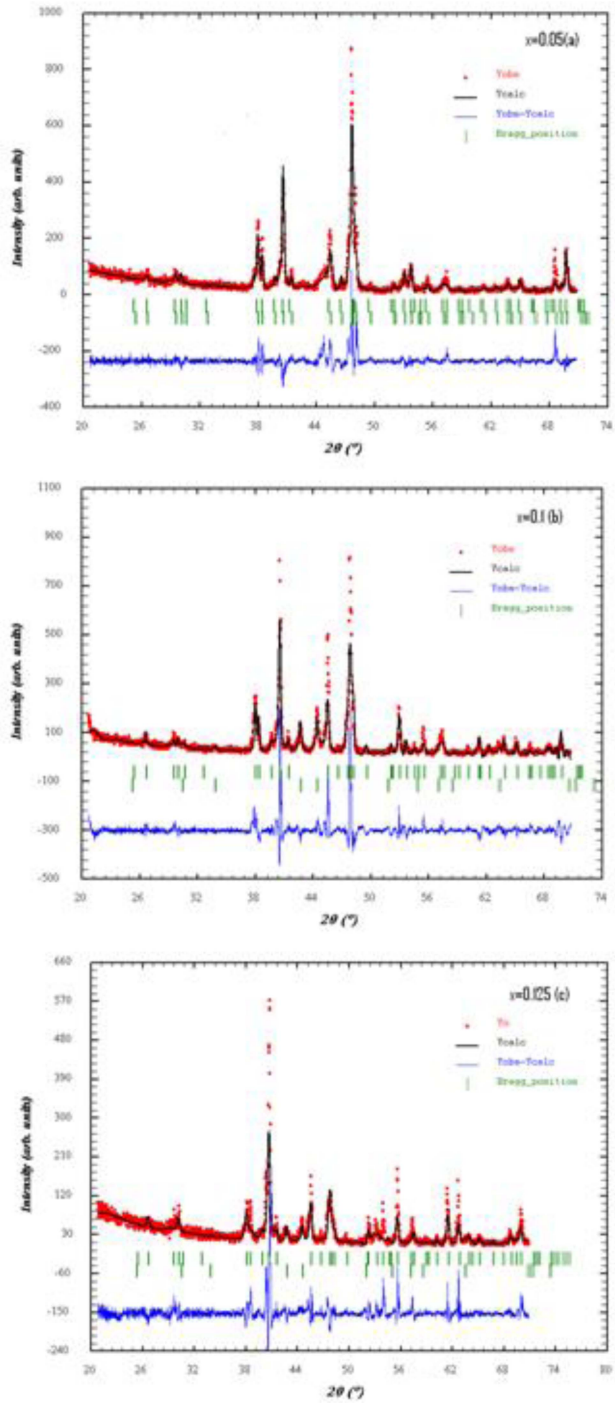


Fig 3. (Color online) X-ray diffraction using CuK_α and Rietveld refinements of $CoMn_{1-x}Cr_xGe$ (x=0.05-0.125) alloys at room temperature.

Figure 4 shows $CoMn_{1-x}Cr_xGe$ (x=0.05, 0.1 & 0.125) orders ferromagnetically below Curie temperature and paramagnetically above this temperature.

The ZFC curve has a slightly lower magnetization value due to the essentially random spatial configuration while cooling through T_C down to low temperatures. At higher

Table 1. Unit cell parameters obtained from Rietveld refinement of $CoMn_{1-x}Cr_xGe$ (x=0.05-0.125) alloys

$CoMn_{1-x}Cr_xGe$	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	V (Å^3)
x=0.05 (Orto I)	5.94454(5)	3.80425(5)	7.02564(5)	90	90	90	158.88 (2)
x=0.05 (Orto II)	5.12374(4)	3.90256(4)	8.13825(3)	90	90	90	162.73 (2)
x=0.10 (Orto)	5.96053(4)	3.80158(4)	7.0197 (3)	90	90	90	159.07 (2)
x=0.125 (Orto)	5.94240(3)	3.81401(3)	7.03225(3)	90	90	90	159.38 (2)
x=0.125 (Hexa)	3.36001(2)	3.36001(2)	5.32187(5)	90	90	120	52.03 (2)

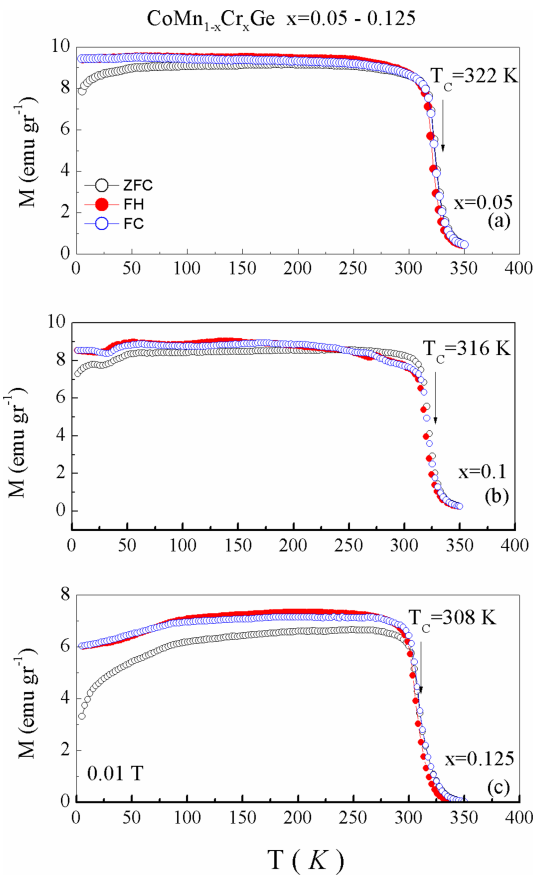


Fig. 4. (Color online) Temperature dependent magnetization data of $CoMn_{1-x}Cr_xGe$ (x=0.05-0.125) alloys in the temperature range of 5 K-350 K in a magnetic field of 100 Oe.

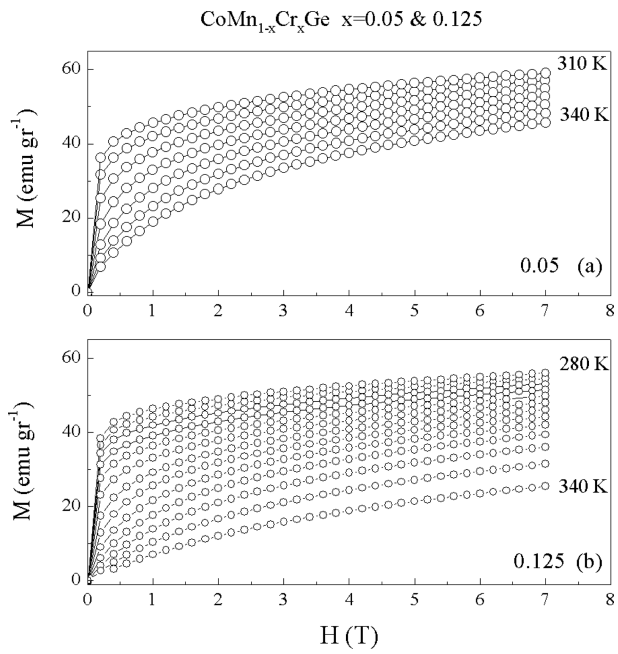


Fig. 5. Isothermal magnetic field dependent magnetization data of $CoMn_{1-x}Cr_xGe$ (x=0.05 & 0.125) alloys up to 7 T.

temperatures, the ZFC and FH curves merge. Isothermal M-H curves of $CoMn_{1-x}Cr_xGe$ (x=0.05 & 0.125) are given in Fig. 5(a) and Fig. 5(b), respectively.

It is clear that magnetic field dependence of magnetization measurements up to 7 T, a metamagnetic transition and magnetic hysteresis is absent from $CoMn_{1-x}Cr_xGe$ (x= 0.05 and 0.125). Therefore, the M(H) curves of $CoMn_{1-x}Cr_xGe$ (x=0.05 and 0.125) indicate that these alloys has only second order phase transition around T_C. Magnetic field dependence of magnetization measurements were performed only for 0.05 and 0.125 since similar magnetic and magnetocaloric behavior was expected for x=0.1 sample.

Furthermore, the Arrott plot has proved to be a useful tool in the analysis and description of magnetic materials [21-23]. The basis of Arrott plot is a Landau description of the magnetization, for which the free energy takes the form

$$F = F_0 - \frac{1}{2}AM^2 + \frac{1}{4}BM^4 - \mu_0 M.H \quad (1)$$

Here A and B are coefficients in a series expansion of the free energy F in powers of the magnetic moment M. $\mu_0 H$ is the external magnetic field and F_0 comprises all contributions that are independent of the magnetic moment M. The free energy may be minimized with respect to M for any external magnetic field H. The result of such a minimization takes the form

$$M^2 = \frac{1}{B}\frac{\mu_0 H}{M} - \frac{A}{B} \quad (2)$$

Arrott plots are obtained by plotting the value of $M(H)$

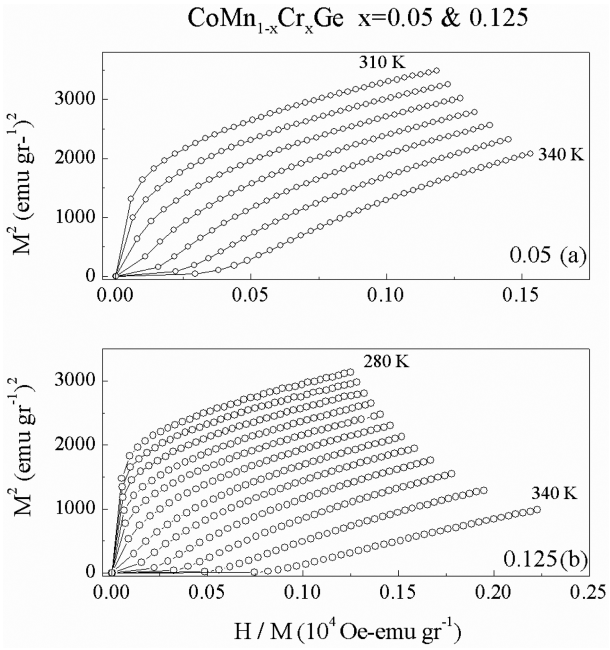


Fig. 6. Arrott plots of the $CoMn_{1-x}Cr_xGe$ (x=0.05 & 0.125) alloys.

and H as a function of M^2 *vs.* $\mu_0 H/M$. According to the above equation, this should result in a straight line. However, for experimental investigations the Arrott plots are often found to result in curved lines. Some physical reasons for the curvature have been given in Ref. 23. The sign of the coefficient B depends on the type of magnetic phase transformation. Therefore, the Arrott plot is a useful tool for judging the type of transformation [24-27]. For the first order transformation (FOT), $B < 0$, an S-shape curve is observed near the transformation temperature. Such an S-shaped curve indicates a negative contribution of some higher order term in the Landau free energy expansion [a negative M^4 term, for instance, i.e., a negative coefficient B in Eq. (2), leads to a negative initial slope of the Arrott plot] [24-27]. While for the second order transformation (SOT), $B > 0$, a straight-line Arrott plot is expected [24-27]. Arrott plots of the investigated compounds are present in Fig. 6(a) and Fig. 6(b), respectively for $CoMn_{1-x}Cr_xGe$ (x=0.05 and 0.125) alloys.

As illustrated, the sample exhibits linear dependence of M^2 *vs.* H/M around T_C, demonstrating a SOT at the transformation temperature for $CoMn_{1-x}Cr_xGe$ (x=0.05 and 0.125) alloys.

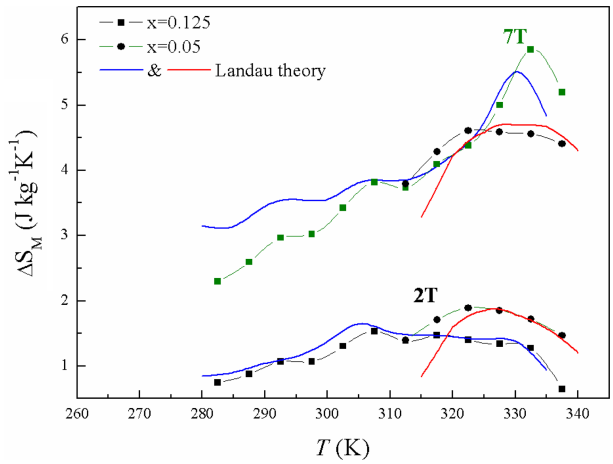


Fig. 7. (Color online) The magnetic field induced entropy change ΔS_M of $CoMn_{1-x}Cr_xGe$ (x=0.05 & 0.125) alloys at 2 T and 7 T magnetic field change. Solid lines show the $-\Delta S_M$ change calculated from Landau theory.

The magnetic field induced entropy change $-\Delta S_M$ of $CoMn_{1-x}Cr_xGe$ (x=0.05 & 0.125) alloys are shown in Fig. 7, which is estimated from the well-known Maxwell relation [1], $q=\int_{T_s}^{T_f} \Delta S_M(T)dT$ by using the data from the M(H) curves.

The maximum value is observed for the x=0.125 sample which is 5.6 J kg^{-1} K^{-1} for the magnetic field change of 7 T. Both samples show conventional magnetocaloric effect. The $-\Delta S_M$ calculated from the Landau relation is also shown in Fig. 7 as solid lines. The results of both methods are in line with one another.

Table 2 shows composition dependence of magnetic transition and structural phase transitions $CoMn_{1-x}Cr_xGe$ (x=0, 0.05, 0.1 and 0.125). The increase of the Cr leads to a decrease of the structural and magnetic phase transition temperature and diminution of the width of the thermal hysteresis. However, there is not a linear dependence of structural and magnetic transition change for the Cr increment shown in phase diagram graph in Fig. 8. Thus, the contribution of both the magnetic entropy and structural

Table 2. Composition dependence of structural phase transitions and ΔT for the $CoMn_{1-x}Cr_xGe$ (x=0, 0.05-0.125) alloys

$CoMn_{1-x}Cr_xGe$	T_C (K)	T^A_s (K)	T^A_f (K)	T^M_s (K)	T^M_f (K)	T^{M-A} (K)	T^{A-M} (K)	ΔT (K)
x = 0 [Ref. 18]	345	429	600	484	384	550	437	113
x = 0.05	322	389	428	376	331	401	356	45
x=0.10	316	364	403	361	327	375	344	31
x = 0.125	308	331	379	350	329	358	335	29

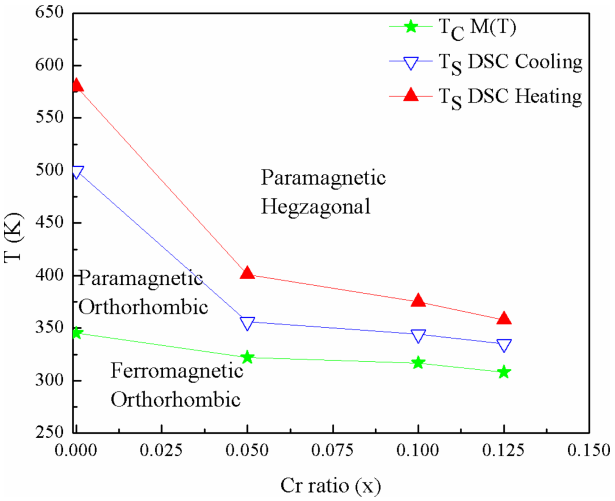


Fig. 8. (Color online) Phase diagram of $CoMn_{1-x}Cr_xGe$ alloys.

entropy to the total entropy change are occurring separately. In each sample, the magnetic phase transition is from a ferromagnetic orthorhombic to a paramagnetic orthorhombic structure. Therefore, this provides to examine the magnetic and structural phase transition contribution to total entropy change separately. The x=0.125 is the best alloy to observe the different contributions of magnetic and structural phase transition, because there are two peaks in x=0.125 alloy, which are at 307 K and 322 K. The magnetic phase transition contribution to entropy change is 3.82 J $kg^{-1}K^{-1}$ at 302 K for 7 T. Meanwhile, the structural phase transition contribution is 5.85 J $kg^{-1}K^{-1}$ at 322 K.

4. Conclusions

In conclusion, we have observed that all Cr doped samples have orthorhombic phase with Pnma space group for low temperatures, while at the same time a hexagonal phase with $P6_3/mmc$ space group for high temperatures. $CoMn_{1-x}Cr_xGe$ (x=0.05, 0.1, and 0.125) shows both structural and magnetic phase transition occurs over room temperature in a wide temperature interval. As the Cr addition increases, both structural and magnetic transition temperatures decrease. The structural phase transition temperature decreases from 550 K to 358 K while the magnetic transition temperature decreases from 345 K to 308 K. However, structural and magnetic transition temperatures are not close to each other. Due to the lack of overlap between magnetic phase transition and structural transition, we observed low entropy change values. The important result is as Cr addition increases, hysteresis sharply decreases from 113 K to 29 K. From Fig. 8 phase diagram graph, it can be concluded that further Cr addition may success overlapping magnetic and structural phase transition to obtain giant magnetocaloric effect. Second order magnetic transition is confirmed by temperature dependent magnetization measurements, entropy change calculation and Landau approximation.

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