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# Magnetic properties and magnetocaloric effect in selected MM'X-type (M, M' = 3d or 4d metal, X = As, P, Ge) and Mn<sub>1-x</sub>T<sub>x</sub>As-type (T = 3d metal) intermetallics

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## Abstract

In this report a review of magnetic properties of two groups of intermetallic compounds in relation with their magnetocaloric effect properties is presented. A first group of materials concerns the MM'X type (M, M'-metal 3d or 4d, X = As, P, Ge) of compounds. In this group the MnRh<sub>1-x</sub>Co<sub>x</sub>As and MnFe<sub>1-x</sub>Co<sub>x</sub>P series of solid solutions are investigated. In a second group of materials, the Mn<sub>1-x</sub>T<sub>x</sub>As (T = Cr, V, Ti, (Ti<sub>0.5</sub>V<sub>0.5</sub>)) series of compounds are analyzed. In this case a special attention is paid for high dc field magnetization measurements and for selected compounds. As a summary the magnetic entropy change vs. M, M' or T transition metal concentration for *F-P* phase transitions will be shown. Furthermore results of KKR-CPA electronic band structure computations in relation to magnetic properties are discussed.

## Introduction

Since the paper published by Tegus et al. [1] concerning giant MCE in MnFeP<sub>1-x</sub>As<sub>x</sub> and MnAs systems, several very interesting series of compounds with different substituted 3d elements were studied. In this report we will consider two of such series: i.e. MM'X and Mn<sub>1-t</sub>T<sub>t</sub>As-types. The MnRh<sub>1-x</sub>Co<sub>x</sub>As isoelectronic system reveals a complex (*x, T*) magnetic phase diagram which evidences several phase transitions between antiferromagnetic *AF* and *AF+F* states [2]. The crystal structure of MnRh<sub>1-x</sub>Co<sub>x</sub>As system is hexagonal of the Fe<sub>2</sub>P-type except for compounds with *x* close to 1 which exhibit the orthorhombic structure of Co<sub>2</sub>P-type. The (*x, T*) magnetic phase diagram was presented first by Chaudouet [2] but a more precise diagram at ambient pressure was reported in following papers [2].

Compounds of the MnFe<sub>1-x</sub>Co<sub>x</sub>P system crystallize with the orthorhombic crystal structure of Co<sub>2</sub>P-type (*SG: Pnma*) [3]. For *x* < 0.5 and *T* < 250 K, the compounds exhibit *AF* properties only, whereas, for *x* > 0.5, both *AF-F* and *F-P* phase transitions are evidenced in the (*x, T*) phase diagram. The *T*<sub>AF-F</sub> phase transition temperature and the *T*<sub>C</sub> decreases and increases vs. the cobalt content, respectively. While *x* > 0.8, the compounds exhibit ferromagnetic properties and high *T*<sub>C</sub> ≈ 500 K is

observed for MnCoP. The transitions exhibit magnetoelastic properties associated with the abrupt changes of lattice parameters, inducing interatomic distances modification [3].

The MCE is also investigated in the vicinity of  $T_C$  in the selected samples in the series of  $Mn_{1-x}T_xAs$  ( $T = Cr, V, Ti, (Ti_{0.5}V_{0.5})$ ) solid solutions in order to quantify the influence of the magnetostructural transition on magnetic entropy jump vs.  $T$  concentration. The following metal contents of the above mentioned systems are chosen for experimental studies. The first one is  $Mn_{1-x}Cr_xAs$  ( $0.01 < x < 0.03$ ), the second one is  $Mn_{1-x}V_xAs$  ( $0.01 < x < 0.03$ ), the third one is  $Mn_{1-x}Ti_xAs$  ( $0.02 < x < 0.3$ ) and finally  $Mn_{1-x}(Ti_{0.5}V_{0.5})_xAs$  ( $0.1 < x < 0.6$ ). The complex  $(x, T)$  magnetic phase diagrams for the above mentioned series of compounds were analyzed first by Zięba and co-workers [4].

## Results and discussion

To cover the desired metal composition regions for MCE analysis several samples are selected. Magnetization measurements are performed in d.c. magnetic field (up to 10 T, 1.5-500 K) at the Institute Néel, CNRS, Grenoble. Two types of experiments are carried out in order to collect isothermal  $M_T(B)$  and isofield  $M_B(T)$  data sets.

The MCE is defined as the thermal response of a magnetic material to the active application of a magnetic field, thus leading to change the temperature of the material. So the MCE of a magnetic material is characterised by either adiabatic variation of temperature ( $\Delta T_{ad}$ ) or isothermal variation of magnetic entropy ( $\Delta S_M$ ). The value of  $\Delta S_M$  can be estimated starting from direct measurements of magnetization versus temperature and applied magnetic field  $M_T(B)$ . Then a numerical integration is performed according to the equation derived from the Maxwell-Weiss formula

$$\Delta S_M = \int_0^B \left( \frac{\partial M}{\partial T} \right)_{B=const} dB \quad (1)$$

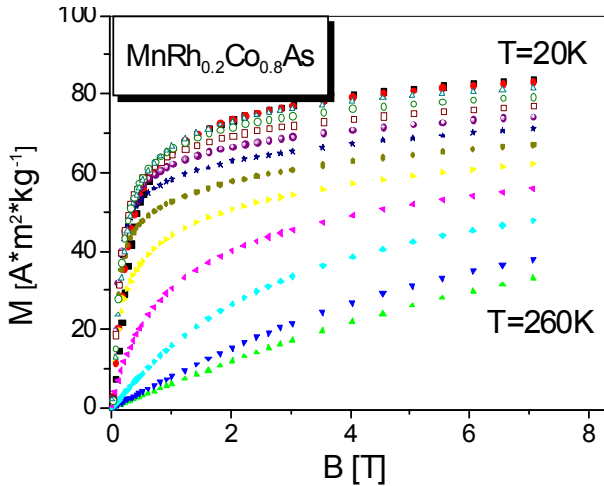


Fig. 1  $M_B(T)$  magnetization curves recorded at 20K – 260 K temperature range. The temperature step between the magnetization isotherms in the figure is 20K.

In Fig.1 the  $M_T(B)$  isothermal magnetization traces vs. applied magnetic field collected in 20–260 K temperature range for  $MnRh_{0.2}Co_{0.8}As$  are shown.  $M_T(B)$  magnetization trace recorded at 20 K shows the evidence of the ferromagnetic state of the studied compound. Similar  $M_T(B)$  runs were also measured for other Co compositions. This behaviour remains in good agreement with the previous magnetization measurements [2]. A 5 K temperature step to record  $M_T(B)$  magnetization curves is applied in our experiments. Using Eq. (1) the MCE amplitudes, for  $x = 0.7$  and  $x = 0.8$  contents are obtained. In Figs. 2a,b temperature dependencies of the magnetic entropy changes are presented. It is worth to note, that a tuning of the Co content allows increasing not only the amplitude of

the MCE (Fig.3), but increases parallel the critical temperature, which seems to be more suitable for room temperature practical applications.

Furthermore, in the case of the  $\text{MnFe}_{1-x}\text{Co}_x\text{P}$  system, showing evidence of complex magnetic structure (as found by neutron diffraction analysis [5]), variation of  $-\Delta S_M$  vs. cobalt content is as well analysed [5].

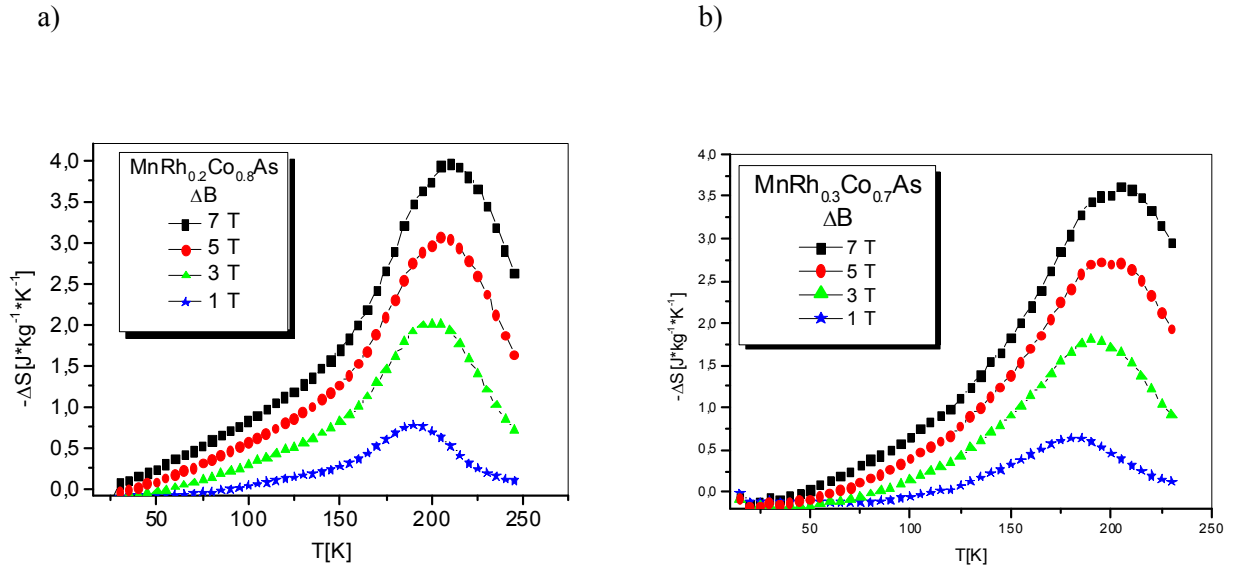


Fig. 2. Magnetic entropy change vs. temperature for (a)  $\text{MnRh}_{0.2}\text{Co}_{0.8}\text{As}$  and (b)  $\text{MnRh}_{0.3}\text{Co}_{0.7}\text{As}$  compounds recorded at different magnetic field jumps.

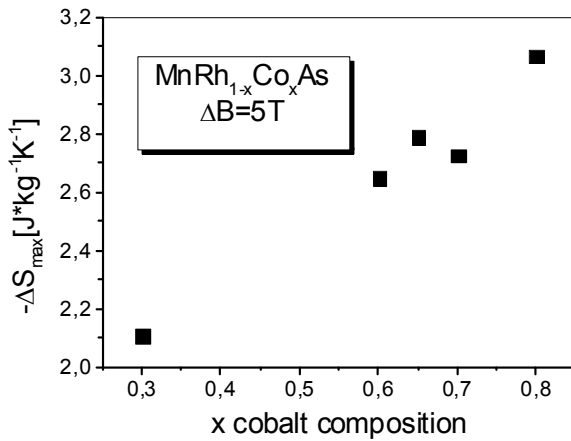


Fig. 3. Magnetic entropy jump vs. cobalt content recorded at 5T.

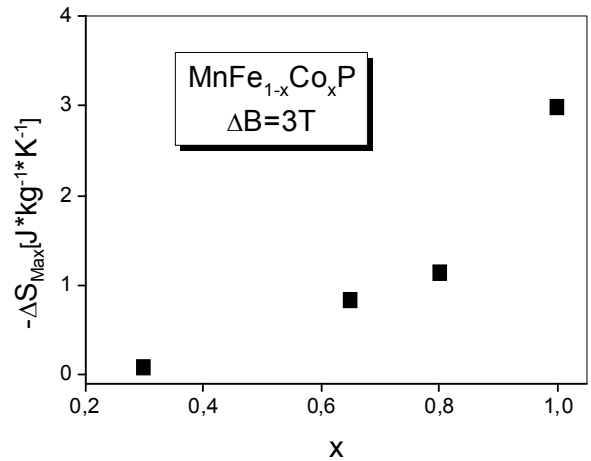


Fig. 4. Composition dependence of magnetic entropy change at  $T_N(x=0.3)$  and at  $T_C$  ( $x=0.65, 0.8, 1.0$ ) for  $\text{MnFe}_{1-x}\text{Co}_x\text{P}$ .

It is concluded that MCE amplitude increases with the increase of Co concentration (Fig. 4).

As the results of the KKR-CPA electronic band structure calculations, performed for the  $\text{MnRh}_{1-x}\text{Co}_x\text{As}$  and  $\text{MnFe}_{1-x}\text{Co}_x\text{P}$  systems, density of state (DOS) for Mn, Fe, Co and Rh atoms are obtained [3,10]. A fair agreement between calculated and experimental values of magnetic moments is found. It should be noted, that in the case of  $\text{MnRh}_{1-x}\text{Co}_x\text{As}$  system the Rh atom practically carries no magnetic moment ( $\mu_{Rh} \approx 0.02 \mu_B$ ), but the Co magnetic moment is found equal to  $\mu_{Co} \approx 0.2 \mu_B$ . This fact should be responsible for the increase of the MCE amplitude in the latter isoelectronic series of solid solutions. It is established for the  $\text{MnFe}_{1-x}\text{Co}_x\text{P}$  system that upon

increasing the Co content, the DOS at the Fermi level strongly decreases, meaning that for high cobalt concentrations the ferromagnetic state is stabilized. We suppose that this fact may be responsible for the increase of the MCE amplitude in the latter series of compounds.

Finally, it should be mentioned, that the  $F$ - $P$  phase transitions observed in the case of  $\text{MnRh}_{1-x}\text{Co}_x\text{As}$  and  $\text{MnFe}_{1-x}\text{Co}_x\text{P}$  series of compounds showed the evidence of the 2<sup>nd</sup> order phase transition.

Here after the magnetocaloric effect of the  $\text{Mn}_{1-x}\text{T}_x\text{As}$  series is analyzed. In this case a strong discontinuous magnetostructural phase transition is observed (at least for small  $x$  values) [4]. It is accompanied by a wide amplitude thermal hysteresis similarly as what was observed in the parent MnAs compound. For instance and for  $\text{Mn}_{1-x}\text{Cr}_x\text{As}$  and  $\text{Mn}_{1-x}(\text{Ti}_{0.5}\text{V}_{0.5})_x\text{As}$  systems a hysteresis widths as large as 13 K ( $x = 0.01$ ) and 15 K ( $x = 0.1$ ) were observed. It is worth to note, that with the increase of the T transition metal concentration, the discontinuous phase transitions transform to 2<sup>nd</sup> order. To determine magnetic entropy change using Eq.(1), the magnetization curves are integrated over magnetic field ranging from 0 to 5 T. In the case of  $\text{Mn}_{1-x}\text{Cr}_x\text{As}$  and for  $x = 0.01$ , value of  $-\Delta S_M$  is found as  $\approx 34.6$  J/kgK. In the case of  $\text{Mn}_{1-x}\text{Ti}_x\text{As}$  the values of  $-\Delta S_M \approx 35$  J/KgK and 16 J/KgK for  $x = 0.02$  and  $x = 0.06$  are obtained, respectively. Moreover, in the case of  $\text{Mn}_{0.99}\text{V}_{0.01}\text{As}$   $-\Delta S_M$  is found equal to 30.5 J/KgK. Finally, in  $\text{Mn}_{1-x}(\text{Ti}_{0.5}\text{V}_{0.5})_x\text{As}$  series  $-\Delta S_M$  is found to be as large as 24 J/KgK and 4 J/KgK for  $x = 0.05$  and  $x = 0.15$ , respectively [6,7]. We conclude that all the studied compounds should be classified as giant MCE materials. Furthermore, the half width of the magnetocaloric amplitude versus temperature increases according to the applied magnetic field for all studied systems. It is worth to note, that the magnetic entropy change versus composition decreases with the increase of T the transition metal concentration on the manganese sublattice. The latter fact is associated with the decrease of amplitude of the magnetostructural phase transition which appears in the MnAs-type solid solutions [7]. In the case of the  $\text{Mn}_{1-x}\text{Fe}_x\text{As}$  system a re-estimate of  $-\Delta S_M$  as associated with the 1<sup>st</sup> order type phase transition was recently proposed in ref. [8]. Such type of analysis based on ref. [11,12] will be as well proposed in a forthcoming paper for the  $\text{Mn}_{1-x}\text{T}_x\text{As}$  systems. Moreover, a phonon mechanism of the magnetostructural  $F$ - $P$  phase transition was discussed very recently by Łażewski et al. [9]. In their paper, the authors have evidenced that the giant coupling between a phonon soft mode and the magnetic moments play the most important role in the magnetostructural phase transition. However no direct theoretical estimation of the MCE amplitude in MnAs was established.

## Conclusions

- 1  $\text{MnRh}_{1-x}\text{Co}_x\text{As}$  and  $\text{MnFe}_{1-x}\text{Co}_x\text{P}$  are interesting MCE materials due to rather large MCE behavior. In both systems the magnetic entropy change increases with the Co contents.
- 2 As the  $\text{Mn}_{1-x}\text{T}_x\text{As}$  ( $T = \text{V}, \text{Cr}, \text{Ti}, (\text{Ti}_{0.5}\text{V}_{0.5})$ ) series is concerned, we conclude that all the studied T compositions can be classified as giant MCE materials. The maximum of magnetic entropy change versus composition decreases with the increase of transition T metal concentration in the manganese sublattice.
- 3 Electronic band structure calculations for  $\text{MnRh}_{1-x}\text{Co}_x\text{As}$  and  $\text{MnFe}_{1-x}\text{Co}_x\text{P}$  were performed and good agreement between calculated and experimental values of total magnetic moments was confirmed. These calculations allow better understanding the increase of the magnetic entropy change vs. the cobalt concentration in both series of solid solutions.

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