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GIANT MAGNETOCALORIC EFFECT IN $Mn_{1-t}(Ti_{0.5}V_{0.5})_tAs$ COMPOUNDS NEAR ROOM TEMPERATURE

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ABSTRACT

$Mn_{1-t}(Ti_{0.5}V_{0.5})_tAs$ compounds with t varying from 0 to 0.20 were synthesised by arc melting and subsequently annealed. The X-ray diffraction analysis reveals pure and fairly crystallised samples. Magnetisation measurements show that the Curie temperature decreases to room temperature with t the substitution rate. The sharp and abrupt character of the 1st order transition of MnAs-type turns to a less marked variation of the magnetic entropy in the vicinity of the transition temperature, profit made to a wider temperature range of MCE efficiency.

INTRODUCTION

MnAs is a compound well known for exhibiting one of the most important magnetocaloric effect due to the exact concomitance of an abrupt crystal structure transformation and a first order magnetic transition [1]. For the pure, stoichiometric and well crystallised binary, the transition was found taking place at T ~ 315 K (42°C), being definitively effective within ΔT ~ 1.5 K, the hysteresis might as large as 20 K. More recently, different attempts were undertaken to shift the transition temperature down closer to room temperature and to reduce as possible the related hysteresis, so expecting to form a giant MCE material having strong potential applications. Obviously three types of chemical modifications are to considered for this purpose:
- off stoichiometry chemical compositions
- substitution of specific element to the non metal site, e.g. when As is partly replaced by another non-metal such as Sb [1].
- substitution of a d-metal to Mn, thus directly influencing the magnetic correlations [2] [3].

In all cases the change in the chemical composition must be as tiny as possible owing to the extremely high sensitivity of the transition in terms of effective Curie temperature, its 1st to 2nd character, the saturation magnetisation and the extend of the hysteresis loop. We have consider the third type of modification because acting directly on the exchange and magneto-elastic forces, also because replacing amount of As by Sb lead to inhomogeneous materials due to segregation effects [4]. In fact we have considered first, substitution of a few percents of all the 3d-metal M (M = Ti, V, Cr, Fe, Co, Ni…) able to replace Mn. If interesting results have been obtained with e.g. Fe, the magnetic ordering temperature being easily shifted to room

temperature (RT) as also reported recently [3], no reduction of the abrupt character of the transition on the contrary can be obtained from Fe substitutions, aiming to reach correspondingly an ideal range of T_C reference to RT.
After series of combinations we have prepared compounds of general formula $Mn_{1-t}(Ti_{0.5}V_{0.5})_tAs$ with $0 \leq t \leq 0.20$, thus combining to preserve the amplitude of the MCE, to shift the order temperature in the close vicinity to RT, and finally to transform the net 1st character of the transition to a 2nd one for a less hysteresis broadening. The choice of the optimised compositions, that must not exceed the value of t = 0.20 to establish a reasonable compromise in between the here above criteria, was based on the knowledge of a phase diagram established by some of us more than fifteen years ago [5].

1 EXPERIMENTAL DETAILS

1.1 Samples preparation

$Mn_{1-t}(Ti_{0.5}V_{0.5})_tAs$ compounds with t = 0, 0.025, 0.05, 0.10, 0.15 and 0.20 were synthesized by the way of solid diffusion reaction. Good purity elements (at least 3N) such as 1/ arsenic scraps, 2/ manganese chips for t = 0, 0.10, 0.20 and manganese powders for t = 0.025, 0.05 and 0.15, 3/ titanium and vanadium powders were mixed altogether in appropriate proportions and finely crushed before heat treatments. The samples were sealed in evacuated in quartz tubes, then heated using a resistive oven. The temperature of treatment was slowly increased up to 800 – 900 °C, depending on the samples, then maintained for 3 days before cooling down. After the samples were homogeneously crushed, they were sealed again in evacuated quartz tubes and annealed for 3 additional days at the same maximum temperature.

1.2 Samples characterisation

The homogeneity, the purity of the samples and their crystal structure were checked using powder X-ray diffraction. For this doing a Siemens D5000 diffractometer was operated in with a graphite monochromator in backscattering mode at either $Cu(K_\alpha)$ or $Co(K_\alpha)$ radiation.
Two types extraction magnetometers developed at the Laboratoire L. Néel, CNRS Grenoble, were utilised to perform systematic magnetic measurements. The first magnetometer allows to work between 1.5 and 300 K under a applied field up to 11 T and the second one allows to work between 290 and 900 K with an field up to 7 T.
Low field (H ~ 0.05 T) magnetisation measurements were performed first to determine the transition temperature. Then, magnetisation measurements versus applied field were performed at low temperature (4 K) in order to well define the magnetic moment at saturation for each samples. Finally, series of magnetisation measurements versus applied field were done around room temperature in order to quantify the magnetic entropy variation versus temperature according to the Maxwell relation:

$$\Delta S_m(T, 0 \rightarrow H) = \int_0^H \left(\frac{\partial M(T, H')}{\partial T} \right)_{H'} dH'$$

2 RESULTS AND DISCUSSION

2.1 Structural characteristics

It is well known that MnAs exhibits a magneto-structural transition from a low-temperature ferromagnetic NiAs-type phase (hexagonal, SG $P6_3/mmc$) to a high-temperature paramagnetic MnP-type phase (orthorhombic, SG Pnma), to which is associated an important magnetocaloric

effect . As well for all the $Mn_{1-t}(Ti_{0.5}V_{0.5})_tAs$ compounds we studied, quite a similar behaviour has been observed [6]. In fact, for the studied samples, X-ray diffraction data as recorded at room temperature show that they are either single NiAs or MnP phase, or even they contain a mixture of these two phases, in specific proportions. No additional phases were found giving an idea of the fairly good purity of the samples. Figure 1 displays two diffraction diagrams obtained with $Co(K_\alpha)$ radiation. Sample with t = 0.15 present a hexagonal NiAs-type structure whereas the one with t = 0.10 presents two picks of the orthorhombic MnP-type structure.

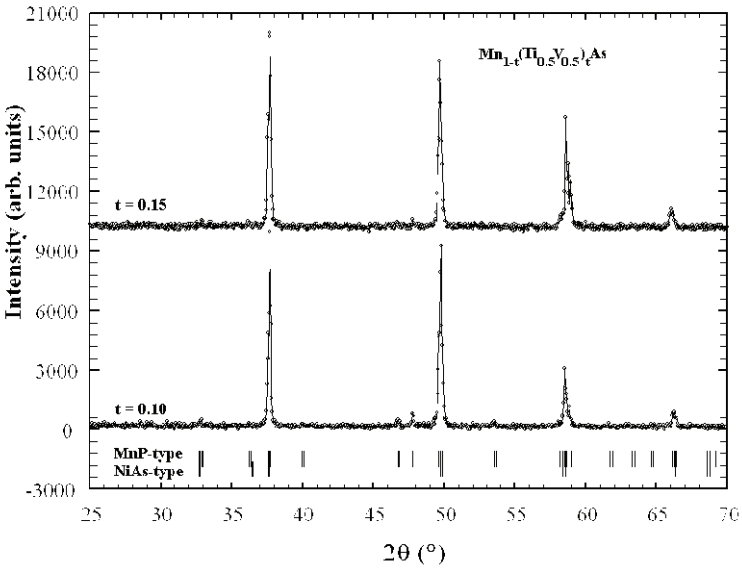

Figure 1: Powder X-ray diffraction patterns recorded at room temperature with $\lambda = Co(K_\alpha)$ for two $Mn_{1-t}(Ti_{0.5}V_{0.5})_tAs$ samples. The tick marks below indicate the position of Bragg reflections for NiAs and MnP structures

2.2 Transition temperatures

The Curie temperature T_c of the ferromagnetic to paramagnetic (F to P) transition was determined from magnetisation versus temperature at low field (0.05 T) measurements. Figure 2 shows an example of these measurements for three of our samples. For t = 0, the transition is very sharp, a characteristic of a 1st order transition. But immediately for other compositions, the transition tends to become smoother. Figure 3 shows the evolution of the Curie temperature with t, the substitution rate of Mn. T_c is defined as the minimum of $\partial M / \partial T$ from the M(T) curves for heating measurements. It decreases from 315 K for t = 0, reaches a minimum at 261 K for t = 0.15, then increases slowly up to 278 K for t = 0.20. The thermal hysteresis is pretty important for these compounds. It increases from 10 K (t = 0) to a maximum of 13 K (t = 0.10), then decrease to 5 K (t = 0.20). This thermomagnetic behaviour confirms the previously reported values obtained by other methods [5] [6].

2.3 Saturation magnetisation

Magnetic measurements at low temperature show the magnetic saturation of the compounds versus an applied field up to 10 T, as shown on Figure 4 with those measurements performed at 4 K. The saturation magnetisation regularly decreases with increasing t. As shown on Figure 5, the corresponding magnetic moment of the metal site linearly decreases by ~ 20% with increasing t up to 0.20. Indeed the magnetic moment of Mn reveals perfectly constant (3.45 μ_B/Mn) within experimental errors, whatever the composition is. This confirm that only

Mn carries a magnetic moment, Ti and V remaining magnetically un-polarized, then acting as diluters in agreement with [5] and as already observed in $Mn_{1-t}Ti_tAs$ [7] [8].

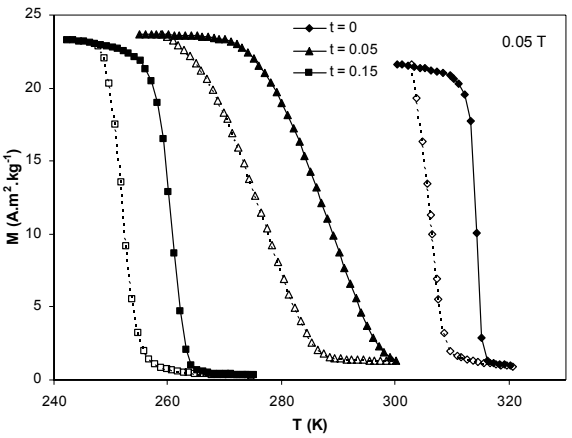

Figure 2: M(T) curves at a field of 0.05 T for the $Mn_{1-t}(Ti_{0.5}V_{0.5})_tAs$ with t = 0, 0.05 and 0.15. Filled symbols are for heating measurements and open ones for cooling ones.

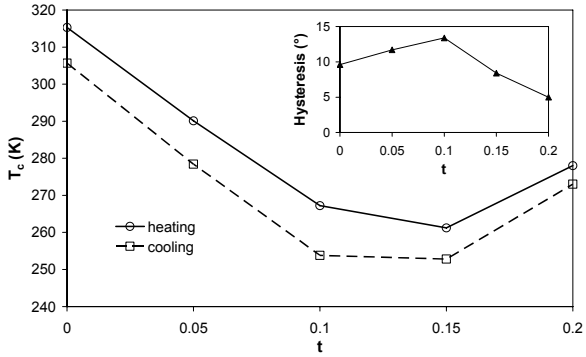

Figure 3: Magnetic transition temperature and hysteresis (inset) as function of composition of $Mn_{1-t}(Ti_{0.5}V_{0.5})_tAs$ (t = 0, 0.05, 0.10, 0.15, 0.20)

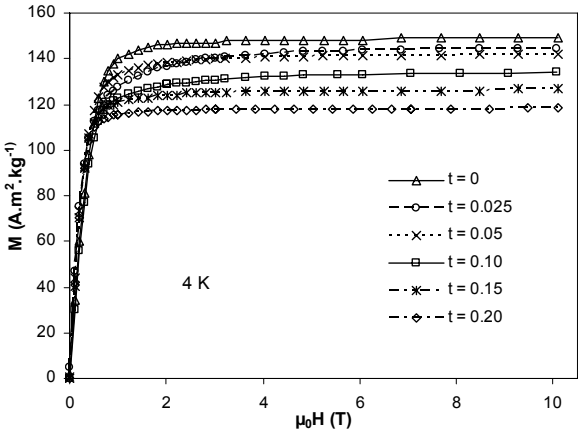

Figure 4: 4 K-magnetisation traces as recorded versus the applied magnetic field for $Mn_{1-t}(Ti_{0.5}V_{0.5})_tAs$ with t = 0, 0.025, 0.05, 0.10, 0.15 and 0.20.

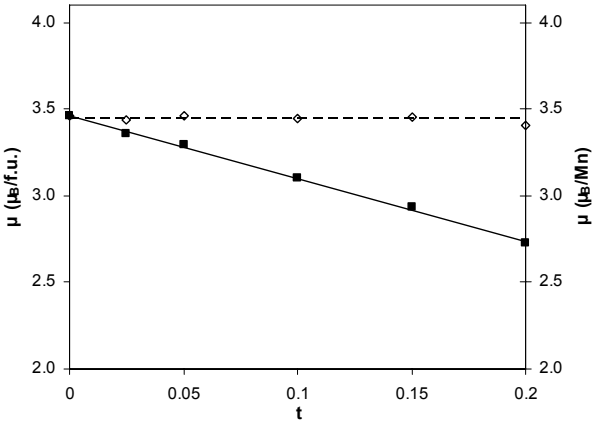

Figure 5: Magnetic moment of the metal site (filled squares) and magnetic moment per Mn atom (open rhombus) as measured at 4 K versus composition

2.4 Isothermal magnetic entropy variation

The magnetic entropy change (ΔS_m) versus temperature was calculated for all compounds applying the Maxwell relation on the magnetic isotherms traces recorded in the vicinity of the transition, as plotted on Figure 6 for $Mn_{0.85}Ti_{0.075}V_{0.075}As$. For an external field varying from 0 to 5 T, the peak values vary drop down from 78 $J.kg^{-1}.K^{-1}$ for t = 0 to 6 $J.kg^{-1}.K^{-1}$ for t = 0.20 (Figure 7). Figure 8 displays the corresponding variation of this maximum with the composition of the compounds. The high peak value of ΔS_m for MnAs is found twice larger than the currently cited one measured by H. Wada [1], but it appears also a third smaller than that recently reported by P. J. von Ranke et al [9].

However, smooth shoulders generally observed apart the main and sharp peak appear with similar amplitudes than those levels reported in the literature. Three typical behaviours of both the shape and the field dependence of ΔS_m were found. A first series of samples, with t = 0, 0.10 and 0.15, exhibit a very sharp peak followed by a high-temperature shoulder. Their traces get rapidly a maximum peak value with the applied field. Two samples, with t = 0.05 and 0.20, exhibit a broad variation of ΔS_m which maximum increases continuously with the applied field. Finally a sample (t = 0.025) exhibit a peak with a low-temperature shoulder, also with a maximum ΔS_m increasing regularly with the applied field.

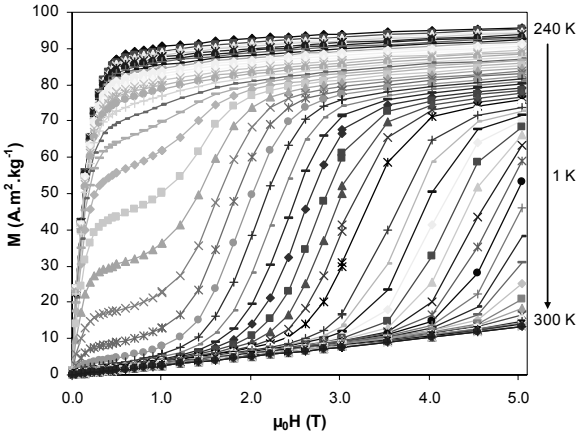

Figure 6: Magnetisation isotherms of $Mn_{0.85}Ti_{0.075}V_{0.075}As$ (t = 0.15) versus magnetic field

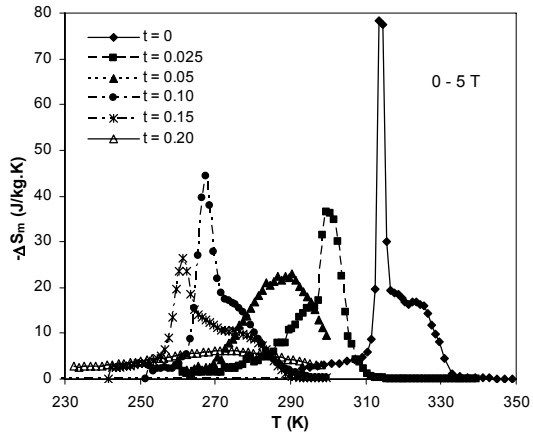

Figure 7: Magnetic entropy variation versus temperature in the magnetic field change from 0 to 5 T for $Mn_{1-t}(Ti_{0.5}V_{0.5})_tAs$

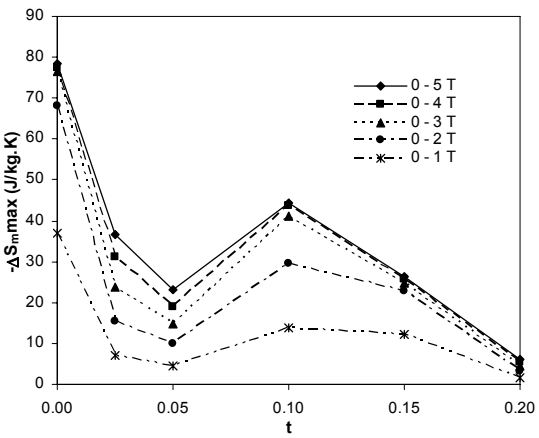

Figure 8: $Mn_{1-t}(Ti_{0.5}V_{0.5})_tAs$ composition dependence of the maximum magnetic entropy variation

The points underlined here above show that the maximum height of the peaks is not a direct criterion to compare the different compounds as shown on Figure 8. Since substituting Mn either by Ti only or by V only leads to different characteristics of the transition as to the variation of T_C reduction with t(Ti,V), it can be anticipated that opposite effects in the coupling forces take place, so leading to an overall non-linear decrease of the peak height. The surfaces integrated under the ΔS_m variation traces reveal a more continuous change of the variation of entropy versus the applied field (Figure 9) or versus the substitution rate (Figure 10). It represents the refrigerating power of

the materials. An upper limit is given by the expression with the total entropy S and the saturation magnetisation at low temperature M_S [10]:

$$\int_0^\infty \Delta S dT = -M_S \Delta H$$

Figure 10 presents the numerically integrated $\Delta S_m(T)$ curves in comparison with theoretical values obtained from saturation magnetisation measurement. Both of these show a comparable decrease with the increase of t. The refrigerating power remains however pretty high and in good accordance with already reported value for MnAs [11]

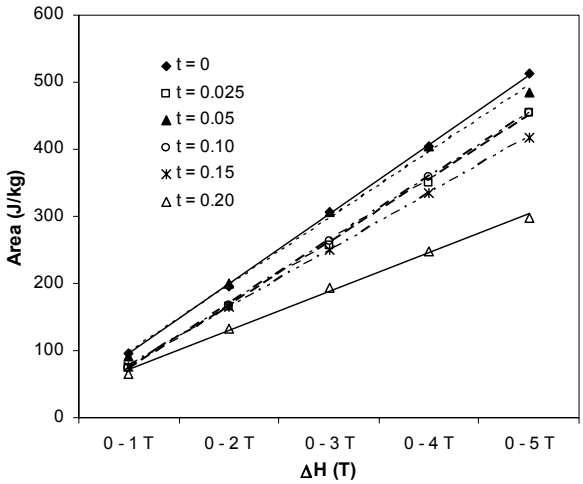

Figure 9: $Mn_{1-t}(Ti_{0.5}V_{0.5})_tAs$ $-\Delta S_m(T)$ peak surface versus the change of magnetic field

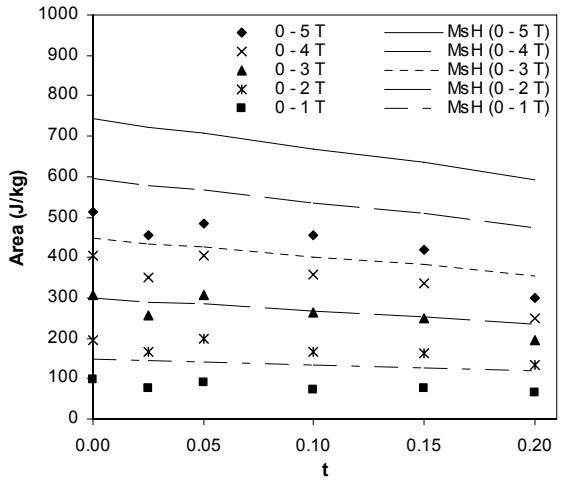

Figure 10: $Mn_{1-t}(Ti_{0.5}V_{0.5})_tAs$ $-\Delta S_m(T)$ peak surface (symbols) and the calculated upper limit $M_S \Delta H$ (lines) versus the t(Ti,V) content

CONCLUSION

The $Mn_{1-t}(Ti_{0.5}V_{0.5})_tAs$ compounds show an important magnetocaloric effect that can be easily adjusted around room temperature by controlling the composition. In particular, compounds with t = 0.05 and t = 0.025 have to be underlined with their maximum of ΔS_m at 290 K and 300 K respectively. The results reported here demonstrate that the $Mn_{1-t}(Ti_{0.5}V_{0.5})_tAs$ series forms potentially excellent candidates for magnetic refrigeration, easily adjustable near room temperature. The reduction of the integrated variation of ΔS_m is rather limited with t, the MCE signal being interestingly temperature range widened.

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