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ANALYSIS AND MODELING OF MAGNETOCALORIC EFFECT NEAR MAGNETIC PHASE TRANSITION TEMPERATURE

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ABSTRACT

Magnetocaloric behavior of gadolinium near room temperature can be correctly described by the Weiss molecular field theory especially in the paramagnetic state. In this paper, this approach is generalized for binary rare earth alloys which present as Gd a second order phase transition. The magnetic entropy variation can be calculated as a function of the temperature and the applied field. This model was tested on a laboratory synthesized samples of Gd-Tb. The agreement between calculations and experiments shows that this model can be easily used for these alloys in order to optimize their composition and adjust their Curie temperatures. For first order transition materials, the observed magnetocaloric effect enhancement can be explained by magnetoelastic effects which are due to the spontaneous crystal deformation and the structure transformation. A model based on the phenomenological approach of Bean Rodbell is developed to describe such a behavior. It highlights the link between the nature of magnetic transition and the magnetocaloric effect. It can be identified by only two parameters: T_0 the Curie temperature without deformation and η an order parameter which characterizes the transition nature. In this paper we apply this model to describe the giant magnetocaloric effect exhibited by the new $Mn_{1-x}(Ti_{0.5}V_{0.5})_xAs$ materials.

INTRODUCTION

Magnetic cooling technology is based on the magnetocaloric effect (MCE), this effect is the result of entropy changes arising from the coupling of the magnetic moment system with the applied magnetic field. When a magnetic field is applied to a material near transition temperature, the magnetic moments become aligned parallel to the magnetic field which causes an increase of the magnetic order and, consequently, a decrease in the magnetic entropy. Under adiabatic conditions, this variation of magnetic entropy is transferred from the magnetic moment subsystem to the atom lattice subsystem, thus leading to an increase the temperature of the material. Suppressing the external magnetic field, the moments become randomly oriented after gaining entropy from the lattice, then the material cools down. This process of heating and cooling caused by variation of an external magnetic field is analogous to the compression and expansion of a gas in classic refrigerator. In order to gain a larger MCE, much attention has been paid to magnetic materials exhibiting first-order phase transformations. In 1997, a giant magnetocaloric effect has been discovered in $Gd_5Ge_2Si_2$ by Pecharsky and Gschneidner [1]. Calculation of the magnetic entropy change ΔS_m using magnetization measurements yielded a value twice larger than for gadolinium, so appearing the material with the best MCE near room

temperature. At T = 276 K and for a magnetic field variation from 0 to 5 T, the magnetic entropy change is ~ 18.5 J/kg.K, a large value resulting both from the first order magnetic phase transition combined with a crystallographic transformation. Later, Tegus et al [2] have shown that $MnFeP_{0.45}As_{0.55}$ possesses a large change of magnetic entropy around 300 K with the same magnitude as $Gd_5Ge_2Si_2$. Once again, the large amplitude of the MCE phenomenon observed for the ternary pnictides results from a first order transition with electronic origin unstabilities of both local magnetic moment and lattices parameters. However, it was shown by Wada et al that MnAs exhibits a giant MCE near T = 318 K [3]. For a change from 0 to 2 T of the applied magnetic field, the resulting magnetic entropy change is ~ 31 J/kg.K. Gama et al [4] reveal that under a pressure of 0.22 GPa and for a magnetic field change from 0 to 5 T the isothermal entropy variation of MnAs is about 267 J/Kg.K which is by far greater than those measured in all mentioned compounds at ambient pressure. More recently, we reported a giant magnetocaloric effect in $Mn_{1-x}(Ti_{0.5}V_{0.5})_xAs$ compounds close to room temperature [5], and besides we demonstrated that the binary rare earth $Gd_{1-x}Tb_x$ alloys [6] are attractive candidates as magnetic refrigerants working near room temperature in an Ericsson cycle. In order to predict or to analyse the MCE in the here reported materials, several models were used. For the rare earth compounds undergoing a second order magnetic phase transition, the MCE was calculated using a model derived from the Weiss molecular mean field theory for ferromagnetic interactions. Based on the Bean and Rodbell model written to explain the first order transition in MnAs [7], a development was made to justify the giant MCE in $Gd_5(Ge_{1-x}Si_x)_4$ [8], $MnAs_{1-x}Sb_x$ [9], and $MnFeP_{0.45}As_{0.55}$ [10]. In this paper, we propose a simpler analysis based of the Bean and Rodbell model [7] to quantify the magnetocaloric effect in the $Mn_{1-x}(Ti_{0.5}V_{0.5})_xAs$ compounds which exhibits a first order transition and in $Gd_{1-x}Tb_x$ alloys where the transition is of second order.

1 EXPERIMENTAL

The sample $Gd_{0.8}Tb_{0.2}$ was prepared by arc melting in an argon gas atmosphere. The compound $Mn_{0.9}Ti_{0.05}V_{0.05}As$, was synthesized by using solid diffusion reaction. For $Mn_{0.9}Ti_{0.05}V_{0.05}As$ (x = 0.1), the pure elements (purity better than 3N) were mixed in appropriate amounts. The sample was heated in sealed evacuated tubes up to 900 °C for 3 days and then crushed and annealed for more 3 days at the same temperature, always in sealed evacuated quartz tube. Magnetization measurements were performed at Louis Néel Laboratory, Grenoble. Magnetic entropy changes were determined from M (H, T) measurements as shown in figure 1, using thermodynamic Maxwell relation:

$$\Delta Sm(T,0-B) = \int_0^B \left(\frac{\partial M}{\partial T}\right)_{B'} dB'$$

For MnAs (x = 0), the experimental data were taken from reference [3].

2 MODEL

According to the Bean-Rodbell model, if the exchange interactions giving rise to the magnetic ordering strongly depends on the interatomic spacing, the Curie temperature T_C is given as follows [7]:

$$T_C = T_0(1+\beta(V-V_0)/V_0) \tag{1}$$

where T_0 is the Curie temperature for a non compressible lattice, V is the volume and V_0 is the volume in the absence of exchange interactions, β is the slope for the volume dependence of T_C. The critical behaviour of the magnetic system is analyzed by using the Gibbs free energy (for an arbitrary angular momentum quantum number J) consisting of the following contributions:

$$G = G_{exch} + G_{Zeeman} + G_{elastic} + G_{entropy} + G_{press} \tag{2}$$

where G_{exch}, G_{Zeeman}, $G_{elastic}$, $G_{entropy}$ and G_{press} represent the exchange interactions, the Zeeman energy, the elastic energy, the entropy term, and the pressure term, respectively. These terms are given below, where N is the number of magnetic atoms per unit volume, k the Boltzmann constant, B the external magnetic field, σ the relative magnetization, M_0 the saturation magnetization, S_m the magnetic entropy, S_r the lattice entropy, K the compressibility coefficient and P the pressure.

$$G_{exch} = -\frac{3J}{2(J+1)} NkT_C\sigma^2 \tag{2a}$$

$$G_{Zeeman} = -BM_0\sigma \tag{2b}$$

$$G_{elastic} = \frac{1}{2K}\left(\frac{V-V_0}{V_0}\right)^2 \tag{2c}$$

$$G_{entropy} = -T(S_m + S_r) \tag{2d}$$

$$G_{press} = P\left(\frac{V-V_0}{V_0}\right) \tag{2e}$$

By inserting (2a) to (2e) into the equation (2) and after minimization with respect to V and σ at $P = 0$, we obtain the dependence of the relative magnetization on the temperature and external magnetic field as already described by Zach et al [11].

$$\sigma = B_J(y) = \frac{2J+1}{2J}\coth\left(\frac{2J+1}{2J}y\right) - \frac{1}{2J}\coth\left(\frac{1}{2J}y\right) \tag{3}$$

where

$$y = \frac{1}{T}\left[3T_0\left(\frac{J}{J+1)}\right)\sigma + \frac{g_J\mu_B J}{k}B + \frac{9}{5}\left(\frac{(2J+1)^4-1}{(2J+2)^4}\right)T_0\eta\sigma^3\right] \tag{4}$$

g_J is the Landé factor, μ_B the Bohr magneton, B_J the Brillouin function and $\eta = \frac{5}{2}\frac{[4J(J+1)]^2}{[(2J+1)^4-1]}NKkT_0\beta^2$ an important term involving K and β, two parameters related to the change of volume. Note that for $\eta < 1$ the magnetic phase transition is 2nd order while for $\eta > 1$ the transition is 1st order. The MCE represented by the magnetic entropy change is calculated from:

$$S_m = R.\left[\ln\left(\frac{\sinh(\frac{2J+1}{2J}y)}{\sinh(\frac{y}{2J})}\right) - yB_J(y)\right] \quad (5)$$

where R is the universal gas constant. The change of the magnetic entropy caused by a variation of magnetic field $\Delta B = B_f - B_i$ is given according to relation (5) by:

$$\Delta S_m(T, \Delta B = B_f - B_i) = S_m(T, B_f) - S_m(T, B_i) \quad (6)$$

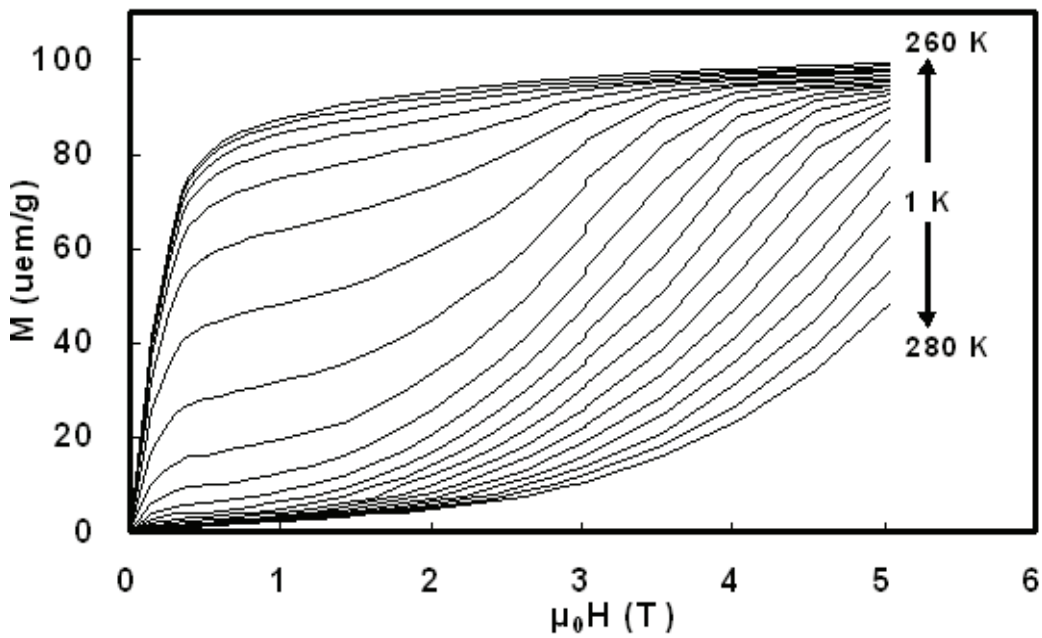

Figure 1: Magnetization isotherms of $Mn_{0.9}Ti_{0.05}V_{0.05}As$ between 260 and 280 K. The step between the isotherms is 1K

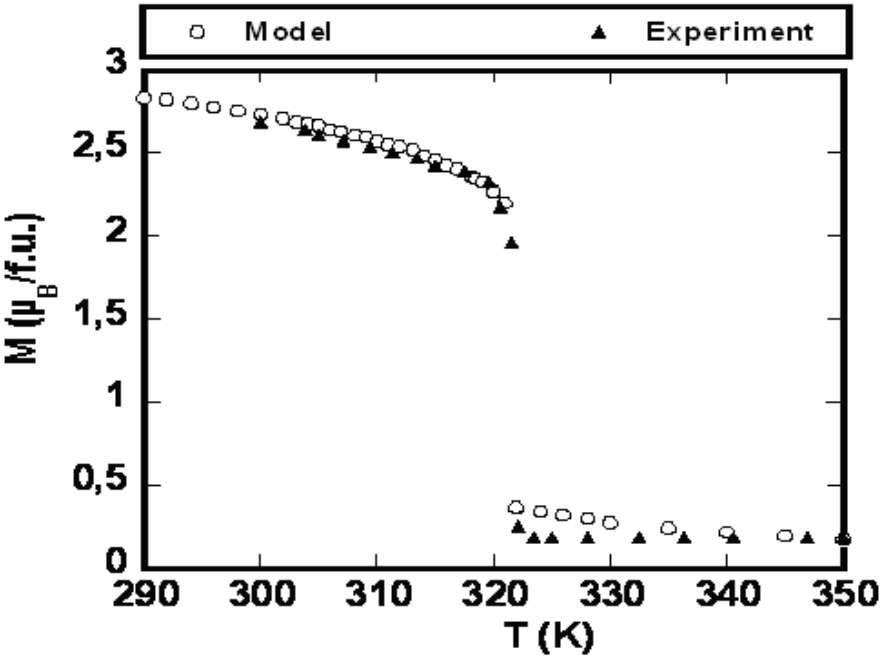

Figure 2: Temperature dependence of magnetization in MnAs under 2 T.

3 APPLICATION OF THE MODEL

On the basis of equations (3) and (4) we can obtain the magnetization versus temperature at constant magnetic field for different values of the parameter η. Thus we can determine the value of η who is in good agreement with the experimental data for calculation of magnetocaloric effect. For $Mn_{1-x}(Ti_{0.5}V_{0.5})_xAs$ series, Landé factor g_J is assumed to be 2 in the equation (3). The effective values of the total angular momentum J are estimated to be 1.7 and 1.65 for x = 0 and 0.1 respectively, values deduced from saturation moments. We have calculated the magnetization versus temperature under different magnetic fields, in order to obtain best parameters for the application of the model. As an example, figure 2 shows the calculated magnetization versus temperature at 2 T in MnAs. Experimental data [3] are also given at 2 T for comparison. The parameters that yield the best fit with the experimental data are $\eta = 2$ and T_0 = 294 K for MnAs, while for $Mn_{0.9}(Ti_{0.5}V_{0.5})_{0.1}As$ $\eta = 2$ and T_0 = 245 K. For MnAs, the obtained parameters are in fair agreement with those determined by P. J. Ranke et al (η = 2, T_0 = 293 K) to calculate entropy change in $MnAs_{1-x}Sb_x$ (x = 0) as reported in reference [9].

Based on the relation (5), the resulting temperature dependences of the calculated magnetic entropy change for x = 0 and 0.1 are displayed in figure 3 for a magnetic field variation from 0 to 2 and 0 to 5 Tesla. For comparison, experimental data are also given for magnetic field varying from 0 to 2 T. Under a magnetic field variation of 2 T, the calculated entropy change in $Mn_{1-x}(Ti_{0.5}V_{0.5})_xAs$ is about 33 J/kg.K at T_C = 318 K for x = 0 and almost 31 J/kg.K at 266 K for x = 0.1. This is in good agreement with the experimental values, where ΔS_m is 32 J/kg.K for x = 0 and about 30 J/kg.K for x = 0.1. Under 2 T, the here reported magnetocaloric effect of $Mn_{1-x}(Ti_{0.5}V_{0.5})_xAs$ series is about twice large as the peak value of $Gd_5Ge_2Si_2$ (14 J/kg.K close to 276 K) and much larger than that obtained in pure gadolinium (~5 J/kg.K) around room temperature. The large magnetic entropy change observed in $Mn_{1-x}(Ti_{0.5}V_{0.5})_xAs$ should be attributed to the

first order phase transition from ferromagnetic to paramagnetic states. This transition is accompanied by brutal changes from the hexagonal NiAs type structure to the orthorhombic MnP type structure. Besides, figure 3 shows that the peak amplitude of the entropy change appears roughly independent of magnetic field, whereas the peak width increases with magnetic field change. This should be explained by the fact that the magnetic field increase makes the transition broader, a characteristic of these types of first order magnetic transitions. However, as shown in figure 3, the Curie temperature of $Mn_{1-x}(Ti_{0.5}V_{0.5})_xAs$ system can be decreased easily from 318 to 266 K by varying x from 0 to 0.1 without significant change in magnetocaloric properties. This result is very important, because by changing the Ti and V content, one can cover a large temperature range and then the materials can be used to design a composite material to be used as magnetic refrigerant. Besides, the particular temperature interval near room temperature in which the composite refrigerant materials can be designed, has a huge technological and industrial interest.

For binary rare earth compounds such as $Gd_{0.8}Tb_{0.2}$, the transition at T_C is of second order, so $\eta = 0$ in equation (4) and the y variable of the Brillouin function presents only the linear term in σ. In this case, the model parameters consisting of Landé Factor, angular momentum and Curie temperature are calculated from Gd and Tb parameters g_J, J and T_C. From these data, the parameters of different Gd-Tb alloys can be evaluated by considering the following relationships deduced from the de Gennes model [12]:

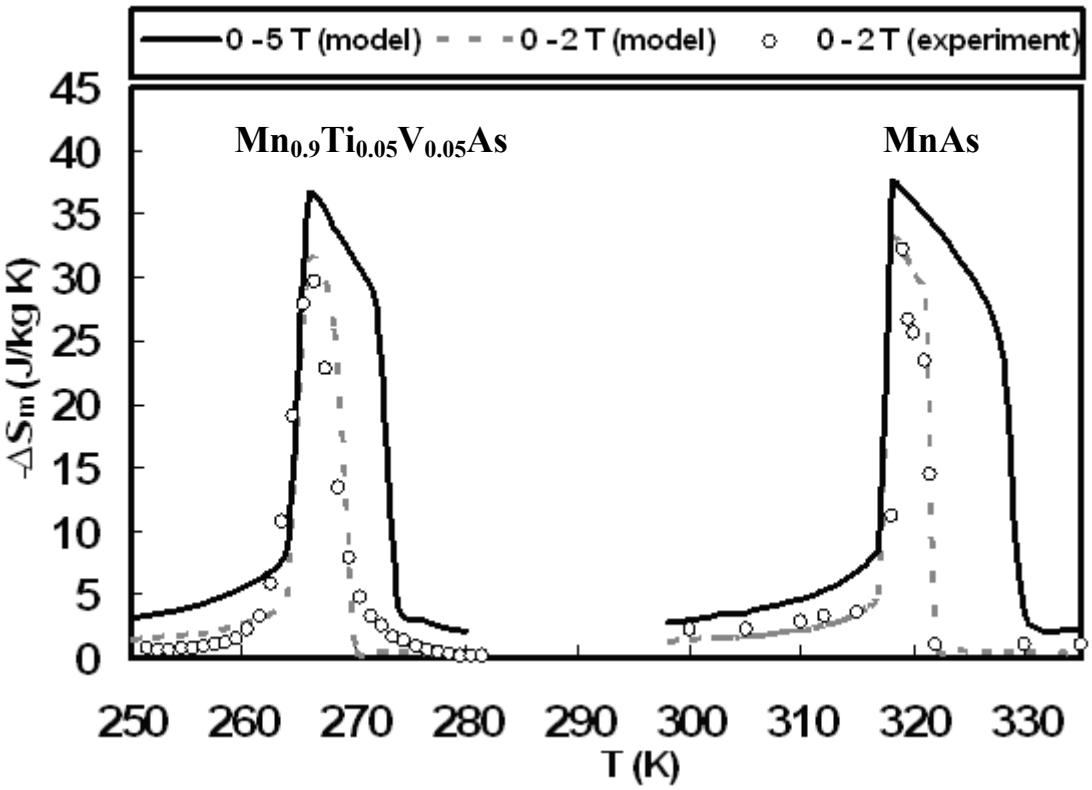

Figure 3: Temperature dependences of the change of magnetic entropy for MnAs and $Mn_{0.9}Ti_{0.05}V_{0.05}As$ compounds upon magnetic field variations of 0-2 and 0-5 T.

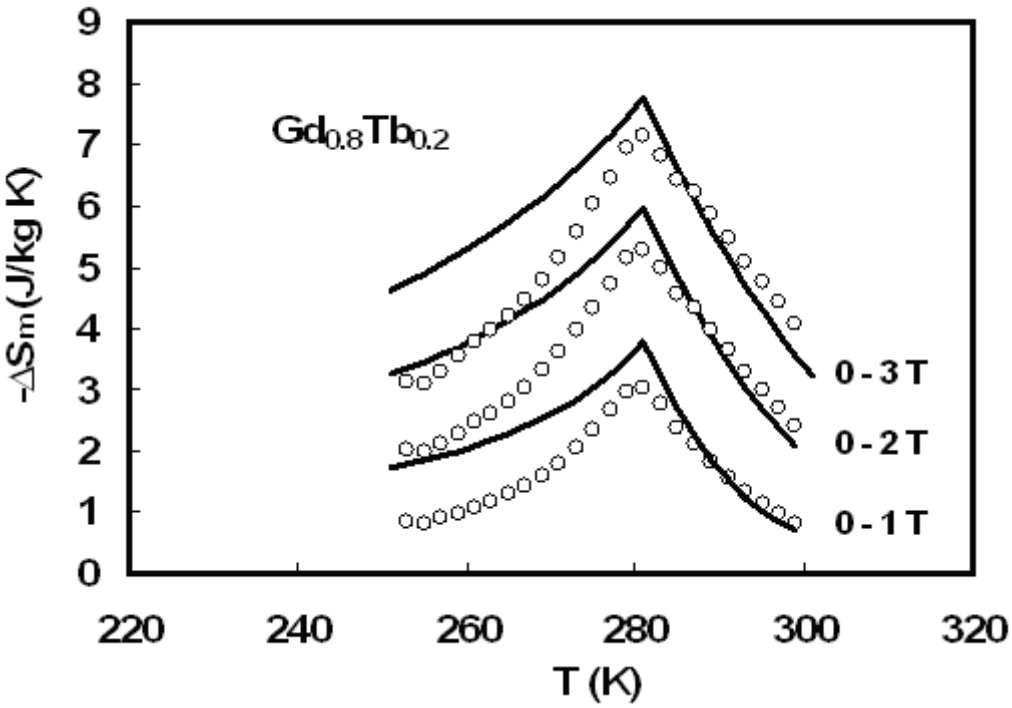

Figure 4: Temperature dependence of the isothermal magnetic entropy change in $Gd_{0.8}Tb_{0.2}$. The solid lines correspond to calculations for a magnetic field change from 0 to 1 T, 0 to 2 T and 0 to 3 T. Open circles represent experimental data.

$$G_{Gd-Tb} = xG_{Gd} + (1-x)G_{Tb} \quad (7)$$

$$\mu_{Gd-Tb}{}^2 = x\mu_{Gd}{}^2 + (1-x)\mu_{Tb}{}^2 \quad (8)$$

Here, $G = (g_J - 1)^2 J(J+1)$ is the de Gennes factor, $\mu = g_J\sqrt{J(J+1)}$ the effective magnetic moment, and x the concentration of Gd in an alloy Gd-Tb. Thus from above equations, one can deduce the corresponding g_J and J for a given alloy. The Curie temperature obeys $Tc = 46G^{2/3}$. Figure 4 presents, the experimental magnetic entropy changes and those calculated from mean field theory of the $Gd_{0.8}Tb_{0.2}$ compound. It can be seen that the experimental and theoretical curves coincide markedly well in the paramagnetic phase. Besides, a significant deviation of theoretical curves from the experimental ones can be observed in ferromagnetic state. This can be due to the inability of the mean field theory to describe accurately well the magnetization at theses temperature ranges ($T < T_C$).

CONCLUSION

In conclusion, the giant magnetocaloric effect in $Mn_{1-x}(Ti_{0.5}V_{0.5})_xAs$ compounds due to a first order magnetic phase transition was analyzed by using the Bean and Rodbell model. With the parameters $\eta = 2$, T_0= 294 K for x = 0 and $\eta = 2$, T_0= 245 K for x = 0.1, the theoretical calculations of the magnetic entropy change versus temperature results are in good agreement with experimental data. The change of x from 0 to 0.1 shifts the Curie temperature from 318 K to 266 K without important change of magnetocaloric properties which is of great interest in magnetic refrigeration applications. For the binary rare earth $Gd_{0.8}Tb_{0.2}$ (η = 0, T_0 = T_C), the theoretical calculations are in rather good agreement with experimental data in particular in the paramagnetic state. Note that, in our model, anisotropy effect characteristic of Tb moments are not taken into account.

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