Calculation of the giant magnetocaloric effect in the MnFeP$_{0.45}$As$_{0.55}$ compound

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We report the theoretical investigations on the giant magnetocaloric compound MnFeP$_{0.45}$As$_{0.55}$. The magnetic state equation used takes into account the magnetoelastic effect that leads the magnetic system to order under first order paramagnetic-ferromagnetic phase transition. The model parameters were determined from the magnetization data adjustment and used to calculate the magnetocaloric thermodynamic quantities. The theoretical calculations are compared with the available experimental data.

I. INTRODUCTION

In the last five years much scientific and technological efforts have been focusing new materials that present the magnetocaloric effect, especially near room temperature, due to the possibility of the use of these materials as refrigerants in magnetic refrigeration.[1,2] The interest in this research area considerably increased since 1976 when G. V. Brown[3] described a near-room temperature magnetic refrigerator, which when compared with conventional gas compression/ expansion engines showed potential advantages in energy savings and elimination of harmful CFCs and HCFCs. However, further improvements were necessary, mainly in refrigerant substances, and in 1997, a giant magnetocaloric effect was discovered[4] in Gd$_5$(Si$_2$Ge$_2$).

Recently, O. Tegus, and co-workers reported the giant magnetocaloric effect in the MnFeP$_{0.45}$As$_{0.55}$ (Ref. 5) compound. Both these materials, Gd$_5$(Si$_2$Ge$_2$) and MnFeP$_{0.45}$As$_{0.55}$, present the essential requirement, for a refrigerant material, of the reversibility of the ferromagnetic-paramagnet phase transition. Also, the origin of the giant magnetocaloric effect is due to the strong first order magnetic phase transition that both materials present. This point can be easily understood by the Maxwell thermodynamic relation that predicts high entropy changes when the magnetization presents discontinuity at the critical temperature. The investigation performed by Morellon *et al.* in Gd$_5$(Si$_{0.45}$Ge$_{0.55}$)$_4$ leads to the conclusion that the magnetic first order phase transition occurs coupled to an orthorhombic-monoclinic crystallographic phase transformation.[6] Differently, in MnFeP$_{0.45}$As$_{0.55}$ the magnetization discontinuity (first order transition) is not associated with a structural transition.

In order to study the origin of the first order magnetic phase transition, Bean and Rodbell[7,8] proposed a model to describe the first order magnetic phase transition considering that the exchange interaction parameter (or Curie temperature in molecular field approximation) is a strong function of the inter-atomic spacing. This model was proposed to explain the experimental evidences of a first order transition in the MnAs compound.[7]

In this work, we theoretically describe the two thermodynamic quantities which characterize the magnetocaloric potential, namely, the isothermal magnetic entropy change, ΔS_{mag}, and the adiabatic temperature change, ΔT_{ad}, observed upon changes of the external magnetic field for the FeMnP$_{0.45}$As$_{0.55}$ compound. The model used is appropriate because of the strong magnetoelastic interactions observed in this compound around the magnetic transition.

The MnFeP$_{1-x}$As$_x$ compounds present hexagonal crystallographic structure for $0.15 < x < 0.66$.[9] Below and above these limits, orthorhombic and tetragonal structures are observed, respectively. In the hexagonal crystallographic phase, decreasing temperature from, e.g., 350 K, three kinds of magnetic phase transitions appear, namely P-AF, P-AF-F, and P-F, depending on the As concentration (here P=paramagnetic, AF=antiferromagnetic, and F=ferromagnetic). The last case, i.e., P-F, occurs in the compound MnFeP$_{0.45}$As$_{0.55}$ to be modeled in this work. The giant magnetocaloric effect is associated to the strong magnetoelastic interaction observed in the temperature dependence of the *a* and *c* hexagonal lattice parameters.[9–11] It is notable that for this compound the magnetic transition, though of first order, is not accompanied by a structural transition, but there are only great and abrupt changes in the values of the lattice parameters, keeping the same crystallographic symmetry. In this case a low hysteresis is expected for the transition, as is observed experimentally, and this is one of the interesting features of this compound for the magnetic refrigeration technology.

In this work the temperature dependence of magnetization was adjusted with the model and the best model parameters were determined. The magnetocaloric effect for the MnFeP$_{0.45}$As$_{0.55}$ compound, expressed as both ΔS_{mag} and ΔT_{ad}, is theoretically predicted and compared with available experimental data on the literature.

II. THE MODEL

The dependence of the exchange interaction on the interatomic distance is phenomenologically considered via the dependence of the critical temperature on the volume change in the following way:

$$T_C = T_0(1 + \beta\omega). \tag{1}$$

In this equation $\omega = (V - V_0)/V_0$ is the cell deformation, β measures the slope of the critical temperature curve on the

cell, and T_0 is the magnetic ordering temperature in the absence of the deformation.

Without external pressure, the Gibbs free energy, for a ferromagnetic system described by the Zeeman effect, distortion and exchange interactions, under the molecular field approximation, is given by

$$G = -\frac{3}{2}\left(\frac{J}{J+1}\right)Nk_B T_C\sigma^2 - Hg\mu_B JN\sigma + \frac{1}{2K}\omega^2 - TS. \tag{2}$$

In this equation J is the ion total angular momentum in the lattice, N is the number of magnetic ions per unit volume, k_B is the Boltzmann's constant, μ_B is the Bohr magneton, $\sigma = M/g\mu_B JN$ is the normalized magnetization at absolute temperature T, g is the Landé factor, H is the external magnetic field, K is the compressibility, and S is the magnetic entropy.

The above free energy minimizes under the deformation

$$\omega = \frac{3}{2}\frac{J^2}{J(J+1)}Nk_B KT_0\beta\sigma^2. \tag{3}$$

Using (3) into (2) and minimizing G with respect to σ, the magnetic state equation is obtained as in Zach and co-workers paper.[12]

$$\sigma = B_J(Y) = \frac{2J+1}{2J}\cot gh\left[\frac{(2J+1)Y}{2J}\right] - \frac{1}{2J}\cot gh\left(\frac{Y}{2J}\right), \tag{4}$$

where

$$Y = \frac{1}{T}\left[3T_0\left(\frac{J}{J+1}\right)\sigma + \frac{g\mu_B J}{k_B}H + \frac{9}{5}\left(\frac{(2J+1)^4-1}{[2(J+1)]^4}\right)T_0\eta\sigma^3\right]. \tag{5}$$

Here B_J is the Brillouin function. The last term in the argument of the Brillouin function comes from the elastic deformation. The parameter η controls the order of the magnetic phase transitions and is given by

$$\eta = \frac{5}{2}\frac{[4J(J+1)]^2}{[(2J+1)^4-1]}Nk_B KT_0\beta^2. \tag{6}$$

From the Landau theory of phase transitions, the condition $\eta > 1$ leads the magnetic system to undergo a first order phase transition. Otherwise, if $\eta < 1$, the second order magnetic phase transition occurs. It is worth noticing that if $\eta = 0$ the relation (4) reduces to the regular magnetic state equation where the Brillouin function presents only the linear term in σ and the magnetic phase transition is always of second order kind and occurs at $T = T_0 = T_C$.

The magnetic entropy can be obtained from the usual relation

$$S_{mag}(T,H;T_0,\eta) = R \cdot \left[\ln(Z) + T\frac{\partial \ln(Z)}{\partial T}\right], \tag{7}$$

where R is the gas universal constant and Z is the partition function which, in our case, is given by

$$Z = \frac{\sinh\left[\left(\frac{2J+1}{2J}\right)Y\right]}{\sinh\left[\frac{Y}{2J}\right]}. \tag{8}$$

The temperature and magnetic field dependence of the magnetic entropy is not trivial, since for a given set of model parameters (T_0, η), the magnetic state equation, $\sigma = \sigma(T,H,\sigma)$, relation 4, must be solved self-consistently.

After the magnetic entropy calculation, the isothermal magnetic entropy changes, ΔS_{mag}, that occur for changes in the external magnetic field, can be directly determined

$$\Delta S_{mag}(T) = S(T,H_2) - S(T,H_1). \tag{9}$$

In order to study the adiabatic temperature change, the lattice entropy, which will be considered in the Debye approximation, must be included in the total entropy, $S_{tot}(T,H)$. The other contributions to the total entropy of the magnetic system will be neglected.

$$S_{tot}(T,H) = S_{mag}(T,H) + S_{lat}(T), \tag{10}$$

with

$$S_{lat}(T) = -3R \ln\left[1 - \exp\left(-\frac{\Theta_D}{T}\right)\right] + 12R\left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T}\frac{x^3 dx}{\exp(x)-1}. \tag{11}$$

In this equation Θ_D is the Debye temperature. The adiabatic temperature change (adiabatic magnetocaloric effect), ΔT_{ad}, that occurs for changes in the external magnetic field is given by

$$-\Delta T_{ad} = T_1 - T_2. \tag{12}$$

This quantity, for a given pair of curves $S_{tot}(T,H_1)$ and $S_{tot}(T,H_2)$, is determined by the adiabatic process condition, $S_{tot}(H_1,T_1) = S_{tot}(H_2,T_2)$.

We used a small piece of $MnFeP_{0.45}As_{0.55}$ to measure the low temperature specific heat, using the relaxation method and a Quantum Design PPMS equipment. From the low temperature part of the measured curve, we obtained a Debye temperature of 158.5 K for the compound.

III. APPLICATION OF THE MODEL

Entering the model parameters η and T_0 into relation (4), the temperature dependence of the magnetization can be calculated for a magnetic system in which the magnetic ion is characterized by the atomic factors g and J. In order to reproduce the saturation magnetization of about 125 Am^2 kg^{-1} reported in Ref. 5, we have put, in relation (4), the external magnetic field $H = 1$ T to be consistent with the experimental data and assumed $J = 3/2$ and $g = 2.48$ as effective values of the total angular momentum and Landé factors of Mn in the crystal. The best model parameters obtained were $\eta = 1.4$ and $T_0 = 296$ K. Figure 1 shows the calculated and the experimental data[5] of the temperature dependence of the magnetization in $MnFeP_{0.45}As_{0.55}$.

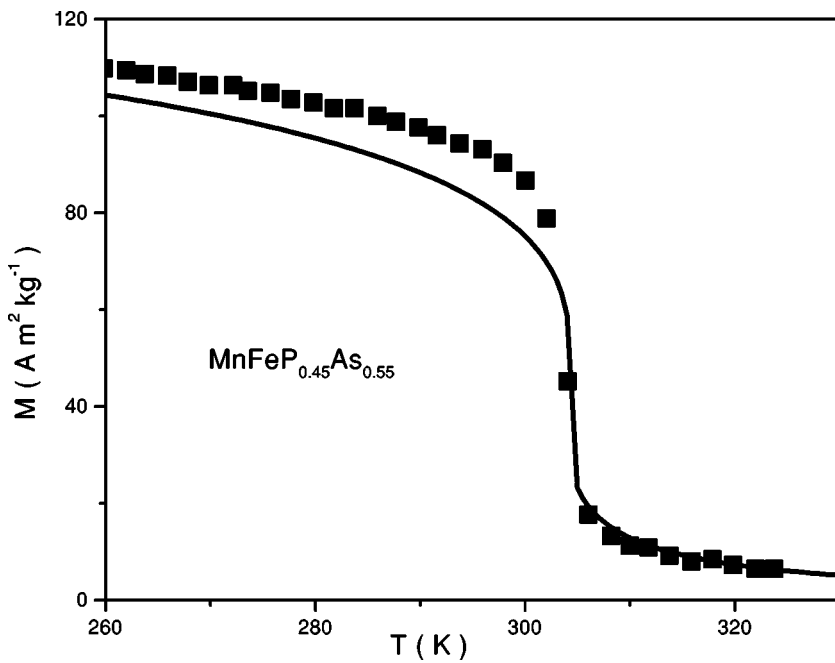FIG. 1. Temperature dependence of magnetization for $MnFeP_{0.45}As_{0.55}$ at $H=1$ T. The solid line represents the theoretical results and the squares the experimental data.

Using the determined η and T_0 model parameters into relation (7) the magnetic entropy versus temperature curve was obtained and the temperature dependence of the ΔS_{mag} curves were constructed for magnetic field changes from 0 to 2 T and from 0 to 5 T, as displayed in Fig. 2. It is worth noticing, in Fig. 2, the good agreement between the theoretical predictions and the experimental data.[5]

From relation (10) the adiabatic temperature change was calculated considering the same model parameters η and T_0 determined above and the Debye formula, relation (11), with the measured Debye temperature $\Theta_D=158.5$ K. Figure 3 shows the temperature dependence of the ΔT_{ad} in the magnetic phase transition region, calculated upon change of external magnetic field from zero to 1, 1.5, 2.0, 2.5 T. Sharp

peaks are predicted to exist near the Curie temperature, which means that the lattice entropy increases (due to the lattice vibration energy) to balance the decrease of the magnetic entropy (due to the alignment of the magnetic ion moments). When the magnetic field is reduced to zero the same ΔT_{ad} is obtained, but with opposite sign (cooling). The experimental data of Tegus[13] on ΔT_{ad} vs T displayed in Fig. 3 was measured with a continuous registration of the temperature change upon fast increase of the applied magnetic field from 0 to 1.45 T. In the temperature region of the magnetic phase transition (300–315 K) the ΔT_{ad} is little sensitive in the changing of the Debye temperature. Note that we do not consider in our model the linear term in specific heat, therefore, the value $\Theta_D=158.5$ K is probably underestimated.
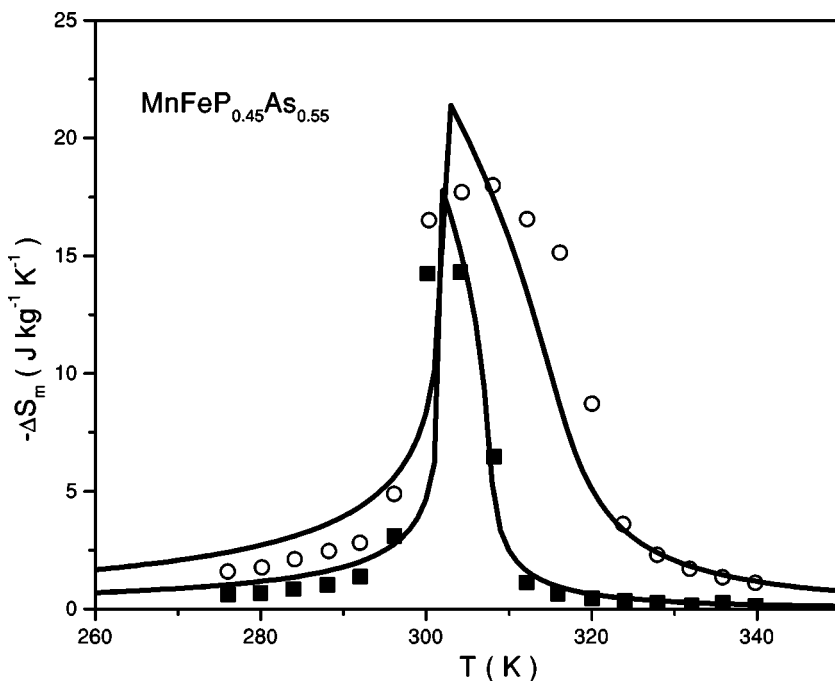

FIG. 2. Temperature dependence of ΔS_{mag} for $MnFeP_{0.45}As_{0.55}$ for magnetic field changes from 0 to 2 T and from 0 to 5 T. The solid lines represent the theoretical prediction and the squares and the open circles show the experimental data from Ref. 5.
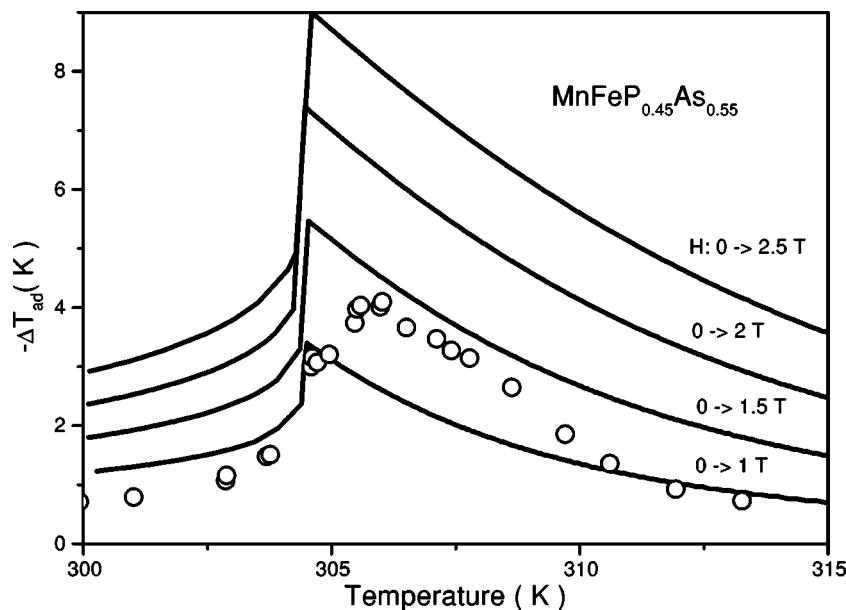
FIG. 3. Theoretical prediction for adiabatic temperature change for $MnFeP_{0.45}As_{0.55}$ upon magnetic field changes from 0 to 1, 1.5, 2, and 2.5 T. The open circles are experimental data from Ref. 13.

However, our calculations show that the values of ΔT_{ad} obtained using variations in the Debye temperature of about $\pm30\%$, i.e., $\Theta_D = 150 \pm 45$ K are almost the same values as that one obtained using $\Theta_D = 158.5$ K. On the other hand, strong influence in ΔT_{ad} as well as in ΔS_{mag} is observed for small changes in the magnetic model parameters η and T_0.

IV. FINAL COMMENTS

The above discussed model, with proper model parameters, can be considered as a good theoretical framework to simulate refrigeration cycles, for example, the Ericsson cycle,[14] for magnetocaloric materials that present P-F first order magnetic phase transition, such as $MnFeP_{1-x}As_x$, $Gd_5(Si_xGe_{1-x})_4$ and $MnAs_{1-x}Sb_x$.[15,16] Using the model parameters $\eta = 1.4$ and $T_0 = 296$ K, the theoretical calculations of the magnetization versus temperature in $MnFeP_{0.45}As_{0.55}$, results show a good theoretical agreement with experimental

data. Our total angular moment $J = 3/2$ (assumed) and gyromagnetic factor $g = 2.48$ (adjusted to fix the experimental saturation moment[5]) are different from those considered by Tegus,[13] namely, $g = 2$ (assumed) and $J = 2$ (estimated from the saturation moment). The calculated magnetocaloric quantities ΔS_{mag} and ΔT_{ad} are in good agreement with the published experimental data.[5]

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