Analytical model to understand the colossal magnetocaloric effect

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We report the theoretical investigations on the colossal magnetocaloric effect using a simple model that couples the lattice entropy and magnetic entropy through the magnetoelastic deformation. Analytical expressions were obtained for the thermodynamic magnetic state equation as well as for the total entropy and heat capacity. The coupled magnetic lattice model predicts high isothermal entropy changes due to the lattice contribution for external magnetic field change, overcoming the magnetic entropy change limit.

INTRODUCTION

Nowadays theoretical and experimental investigations on the new magnetocaloric materials constitute one of the areas of larger interest in condensed matter physics.[1] The historical mark in this research area was the discovery of the giant magnetocaloric effect in the $Gd_5(Si_xGe_{1-x})_4$ alloys in 1997 by Pecharsky and Gschneidner.[2] Using alloys from this pseudobinary system, the giant magnetocaloric effect can be produced in a large temperature interval from ∼20 to ∼290 K by adjusting the Si:Ge ratio, and can be utilized as refrigerant material in magnetic refrigerator.[3] More recently, other giant magnetocaloric materials were discovered, e.g., $MnAs_{1-x}Sb_x$ by Wada *et al.*,[4,5] $MnFeP_{0.45}As_{0.55}$ by Tegus *et al.*,[6] and $La(Fe_{1-x}Si_x)$ and its hydrides.[7,8] The origin of the giant magnetocaloric effect in the above materials is due to a first order magnetic phase transition which leads to a high change (discontinuity) in the order parameter (magnetization) and therefore a high change in the isothermal magnetic entropy change ΔS and in the adiabatic temperature change ΔT_{ad}. These two thermodynamic quantities depend on temperature and are measured upon magnetic field change.

Theoretical microscopic models have been applied with success to explain the so-called conventional magnetocaloric effect (associated with second order magnetic phase transition). For example, the anomalous magnetocaloric peak in $(Dy_{1-z}Er_z)Al_2$ in the concentration range $0.15<z<0.5$ was fully explained using a Hamiltonian that includes the crystalline electrical field interaction.[9] The influence of the giant quadrupolar interaction leads the YbAs compound to cool upon magnetizing and warm upon demagnetizing in the temperature range between 33 to 84 K (anomalous magnetocaloric effect).[10] The experimental data[11] of ΔT_{ad} and ΔS in $ErCo_2$ and $Er_{0.8}Y_{0.2}Co_2$ were explained considering the localized and itinerant magnetic contributions to the entropy.[12] Nevertheless, the theoretical investigations on the giant magnetocaloric materials (nonconventional magnetocaloric effect) are just beginning. As far as we know, the first thermodynamic discussion about the magnetocaloric effect, generated by the first order magnetic transition, was qualitatively accomplished by Pecharsky and co-workers.[13] Re-

cently, studies considering a proper magnetic state equation (that takes into account the microscopic parameters and the possibility of the ferromagnetic-paramagnetic first order transition) were used to adjust (in a self-consistent way) the giant magnetocaloric effect measured in $Gd_5(Si_xGe_{1-x})_4$ (Ref. 14), $MnAs_{1-x}Sb_x$ (Ref. 15), and $MnFeP_{0.45}As_{0.55}$ (Ref. 16).

One of the main characteristics of the giant magnetocaloric materials, cited above, is the coexistence of the first order magnetic phase transition with a high variation in the lattice parameter or in the volume of the crystalline cell. The variation of the lattice parameter drives a variation in the lattice-elastic energy which, in the equilibrium condition, must be counterbalanced by the exchange energy among the magnetic ions (which Néel called exchange magnetostriction[17]). In the materials with relevant exchange magnetostriction, it is expected to find a strong dependence of the exchange parameter with the volume (or lattice parameter). In the mean field approach (where the exchange parameter is proportional to the Curie temperature) we can describe that behavior using the linear dependence of the Curie temperature on the lattice deformation, as was proposed in the Bean and Rodbell model.[18] In the context of the magnetocaloric effect the lattice entropy plays a role as important as the magnetic entropy, since in the adiabatic process the increase (or decrease) in magnetic entropy (due to a change in external magnetic field) forces a decrease (or increase) in lattice entropy when we neglect all other entropy change contributions. In general, the lattice is treated in the Debye assumption, where the Debye temperature is considered constant[19] or, in some models, as an implicit temperature function,[20] which is a good theoretical framework to deal with the conventional magnetocaloric effect. Nevertheless, for giant magnetocaloric materials (where high cell deformation occurs) the more detailed analysis of lattice vibrations is of great importance because of its bearing on with the crystalline cell deformation. As the Curie temperature changes with the lattice parameters it is expected that the Debye temperature is also influenced by the lattice parameters. In this paper we extend the Bean and Rodbell model, including a phenomenological linear lattice deformation dependence of the Debye

temperature. The general magnetic Gibbs energy was constructed, and from it analytical expressions for the magnetic state equation, heat capacity, and entropy were obtained and applied in the study of the magnetocaloric quantities ΔT_{ad} and ΔS. The goal of the systematic study of the magnetocaloric quantities as a function of model parameters, presented in this work, is not to adjust a particular magnetocaloric material, but to bring about a more detailed understanding of the role of lattice entropy when it depends on the magnetic state through lattice deformation, in a self-consistent way.

The strong motivation for this work was to understand the theoretical physical origin of the recently discovered colossal magnetocaloric effect in MnAs by Gama *et al.*[21] Measurements on MnAs under pressure obtained values up to $\Delta S = 267$ J/(kg K), far greater than the magnetic limit arising from the assumption of magnetic field independence of the lattice entropy contribution to the magnetocaloric effect.

THEORY

The total entropy of the magnetic material will be considered constituted by the magnetic and lattice components which in general depend on temperature, magnetic field, and volume:

$$S(T,H,V) = S_M(T,H,V) + S_L(T,H,V). \tag{1}$$

In an isobaric process, the total entropy and the free energy changes are given by

$$dS = \left(\frac{\partial S}{\partial T}\right)_{H,V} dT + \left(\frac{\partial S}{\partial H}\right)_{T,V} dH + \left(\frac{\partial S}{\partial V}\right)_{T,H} dV, \tag{2}$$

$$dF = \left(\frac{\partial F}{\partial T}\right)_{H,V} dT + \left(\frac{\partial F}{\partial H}\right)_{T,V} dH + \left(\frac{\partial F}{\partial V}\right)_{T,H} dV$$
$$= -SdT - MdH - PdV, \tag{3}$$

where M is the magnetization. Since the free energy is a state function, the amount by which the state variables change must be independent of the path taken, so mathematically relation (3) corresponds to an exact differential which leads to the following Maxwell relations:

$$\left(\frac{\partial P}{\partial H}\right)_{T,V} = \left(\frac{\partial M}{\partial V}\right)_{T,H}, \tag{4}$$

$$\left(\frac{\partial S}{\partial V}\right)_{T,H} = \left(\frac{\partial P}{\partial T}\right)_{H,V}, \tag{5}$$

$$\left(\frac{\partial M}{\partial T}\right)_{H,V} = \left(\frac{\partial S}{\partial H}\right)_{T,V}. \tag{6}$$

Putting Eq. (6) into relation (2), we got for an isochoric-isothermal process, that the total entropy change due to the change in external magnetic field from H_1 to H_2 is given by

$$\Delta S = \left(\frac{\partial M}{\partial T}\right)_H dH \approx \frac{1}{\Delta T} \int_{H_1}^{H_2} [M(T + \Delta T) - M(T)] dH. \tag{7}$$

We must *bear in mind* that the above relation represents the total isothermal entropy change if the total entropy does not depend on volume change, since it was obtained keeping fixed the volume, see relation (6). Therefore, if the total entropy depends on the volume change, the proper way to write ΔS is given by

$$\Delta S \approx \frac{1}{\Delta T} \int_{H_1}^{H_2} [M(T + \Delta T) - M(T)] dH$$
$$+ \{S[V(H_2)] - S[V(H_1)]\}. \tag{8}$$

The second term in relation (8) can have great importance for a magnetocaloric material which presents a strong magneto-elastic interaction, and can be neglected otherwise. Note that if we were using the full Gibbs free energy, the Maxwell relations expressed in relations (4)–(6) would be at constant pressure, as is usually encountered in experimental conditions. But in the case of theoretical calculations, it is far easier to use the Helmholtz free energy for the deformation term, as we did above. In this case the Maxwell relations are expressed at constant volume, and to take into account this condition, it is necessary to add the second part of Eq. (8). If this is not done, the calculations will result in an incorrect amount for the entropy variation, as will be better discussed below.

We propose a simple model to understand the limitation of relation (7). From now on, we will call this model as the coupled-magnetic-lattice model (CMLM). The CMLM is based on the Bean and Rodbell model.[18] Basically, the Bean and Rodbell model consider the dependence of the exchange interaction on the interatomic distance. This dependence is phenomenologically described by considering the dependence of the critical magnetic phase transition temperature on the volume change in the following way:

$$T_C = T_0(1 + \beta\omega). \tag{9}$$

Here $\omega = (V - V_0)/V_0$ is the volume change (cell deformation), $\beta = d(T_C/T_0)/d(V/V_0)$ measures the slope of the critical temperature curve on the volume change and T_0 is the ordering temperature in the absence of the lattice deformation. In CMLM the lattice entropy is connected to the magnetic lattice through the Debye temperature Θ dependence on deformation

$$\Theta = \Theta_0(1 - \gamma\omega), \tag{10}$$

where Θ_0 is the Debye temperature in the absence of lattice deformation and γ is the Grüneisen parameter, Refs. 22, 23, and 24.

The generalized magnetic Gibbs free energy, per volume, for the CMLM is written as

$$G = -HM_s\sigma - \frac{1}{2}Nk_BT_C\sigma^2 + \frac{1}{2K}\omega^2 - T(S_M + S_L) + P\omega, \tag{11}$$

where N is the number of magnetic ions per unit volume, k_B is the Boltzmann's constant, and $\sigma = M/M_s$ is the normalized magnetization at absolute temperature T and magnetic field H. The pressure and the compressibility are represented by P

and K, respectively. Note that we are considering magnetic ions of spin $\frac{1}{2}$ for simplicity, so $M_s = N\mu_B$.

The lattice and magnetic entropy (for spin $\frac{1}{2}$) are given by

$$S_L = -3R\ln\left[1 - \exp\left(-\frac{\Theta}{T}\right)\right] + 12R\left(\frac{T}{\Theta}\right)^3 \int_0^{\Theta/T} \frac{x^3 dx}{\exp(x) - 1}$$

$$+ \frac{V_0\alpha}{K}\omega, \tag{12}$$

$$S_M = R\left[\ln(2) - \ln(1 - \sigma) - \frac{(1 + \sigma)}{2}\ln\left(\frac{1 + \sigma}{1 - \sigma}\right)\right], \tag{13}$$

where R is the gas universal constant and α is the thermal expansion coefficient. This coefficient appears since the lattice entropy is not evaluated at constant volume, therefore, the thermodynamic relation $C_P - C_V = \alpha^2 VT/K$, between heat capacity at constant pressure and volume is taken into account. V is the molar volume of the material (atomic weight/density).

For $T > \Theta$, the lattice entropy can be approximated by the expression

$$S_L = 3R[\ln T - \ln \Theta + 4/3] + \frac{V_0\alpha}{K}\omega. \tag{14}$$

Figure 1 displays the lattice entropy vs temperature, without thermal expansion, using relation (12) for $\Theta = 200$ K (full line). The dotted line represents the entropy considering the approximate relation (14). In this figure we are considering $\gamma = 0$. Note that for $T > \Theta = 200$ K both expressions present almost the same results.

The deformation that minimizes relation (11) is given by

$$\omega = \frac{1}{A}\left[\left(\frac{\eta}{3\beta}\right)\sigma^2 + \left(\alpha + \frac{3RK\gamma}{V_0}\right)T - PK\right] \tag{15}$$

where $A = [1 - (3RK\gamma^2/V_0)T]$ and $\eta = (3/2)Nk_BT_0\beta^2$.

Substituting relation (15) into relation (11) and taking the derivative with respect to σ, an analytical expression for the magnetic state equation is obtained:
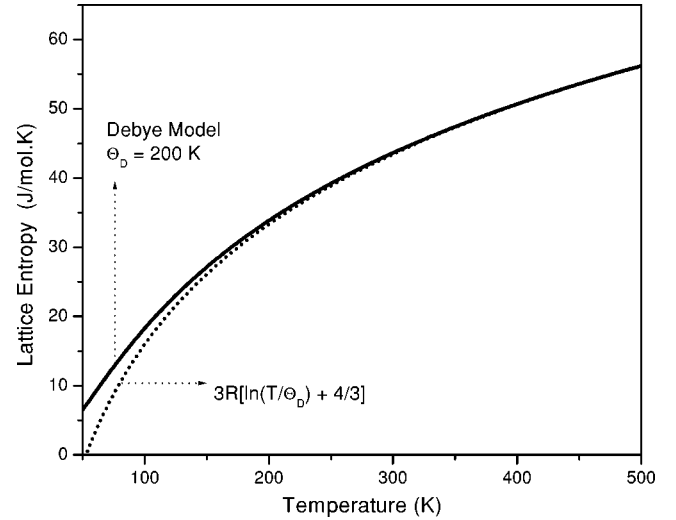

FIG. 1. Temperature dependence of lattice entropy for $\Theta_D = 200$ K, full line. The dotted line represents the approximation for lattice entropy given by relation (14), with $\alpha = 0$.

$$\sigma = \tanh\left[\frac{\mu_B H}{k_B T} + \frac{T_0}{T}(1 + \beta\omega)\sigma\right]. \tag{16}$$

Note that the argument in the hyperbolic tangent is not linear in σ since ω depends on σ, see relation (15). In this way, a first order magnetic phase transition occurs for $\eta > 1$ in the absence of pressure, as well described in literature.[14] In our CMLM, the magnetic state equation is connected to the lattice through the Grüneisen parameter.

From the total entropy, in the assumptions stated above, an analytical expression is obtained for the total heat capacity:

$$C = R\left(\frac{\mu_B H + k_B T_0}{k_B T}\right)\Delta + \frac{1}{A}\left[\frac{3R\gamma}{1 - \gamma\omega} + \frac{V_0\alpha}{K}\right]$$

$$\times\left[\left(\alpha + \frac{3RK\gamma}{V_0}\right)T - \frac{2\eta\sigma}{3\beta}\Delta\right] + 3R, \tag{17}$$

where

$$\Delta = \frac{\left[\mu_B H + k_B T_0\left[\left(1 - \frac{\beta PK}{A}\right)\sigma + \frac{\eta}{3A}\sigma^3\right]\right]\sec h^2\left(\frac{\mu_B H}{k_B T} + \frac{T_0}{T}(1 + \beta\omega)\sigma\right)}{k_B\left[T - T_0\left(\frac{2\eta\sigma^2}{3A} + \beta\omega + 1\right)\sec h^2\left(\frac{\mu_B H}{k_B T} + \frac{T_0}{T}(1 + \beta\omega)\sigma\right)\right]}.$$

Note that the temperature and magnetic field<> dependence of the heat capacity as well as the total<> entropy must be calculated self-consistently with the magnetic state equation, relation (16), since these thermodynamic quantities depend on the magnetization. From the total entropy, the

magnetocaloric effect is directly determined by the following relations:

$$\Delta S = S(H, T) - S(H = 0, T) \tag{18}$$

and

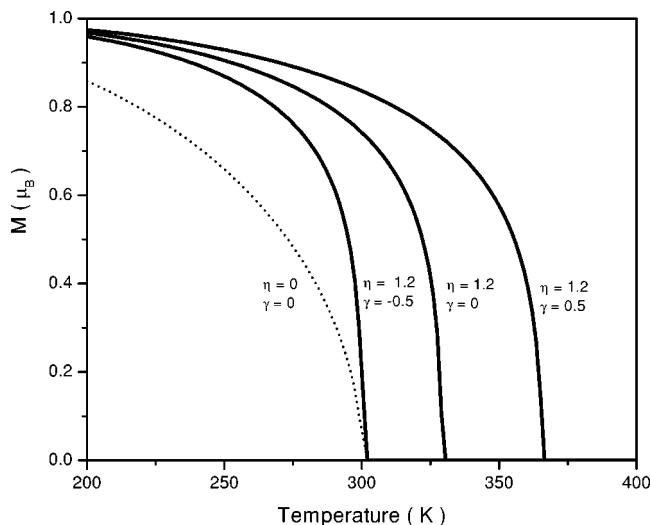FIG. 2. Magnetization versus temperature for different model parameters sets considered in the text.

$$\Delta T = T_2 - T_1, \tag{19}$$

where the entropy change ΔS is considered in an isothermic process and the temperature change ΔT is obtained in an adiabatic process by solving the adiabatic equation $S(H, T_1) = S(H=0, T_2)$.

Using our model magnetic state equation (16) with the total entropy it is easy to check the Maxwell relation (6), and to obtain the analytical volumetric contribution to the total entropy change

$$[S(\omega_2) - S(\omega_1)] = 3R \ln\left(\frac{1 - \gamma\omega_1}{1 - \gamma\omega_2}\right) + \frac{V_0\alpha}{K}(\omega_2 - \omega_1)$$

$$= S_L(\omega_2) - S_L(\omega_1), \tag{20}$$

where $\omega_i = [V(H_i) - V_0]/V_0$.

Systematic parametric investigations were performed on the spontaneous ($H=0$) temperature dependence of the magnetization as shown in Fig. 2. Four sets of model parameters were considered, namely, set 1 ($\eta=0, \gamma=0$), set 2 ($\eta=1.2, \gamma=0$), set 3 ($\eta=1.2, \gamma=0.5$), and set 4 ($\eta=1.2, \gamma=-0.5$). Set 1 gives the simple Brillouin function shape, dotted line, where $T_0=300$ K and $P=0$ were taken for all curves. Set 2 introduces the magnetoelastic effect on the magnetic state equation and leads to a first order magnetic phase transition with an increase in the Curie temperature. Fixing $\eta=1.2$, the role of the γ parameter is to reduce or increase the Curie temperature, depending on the negative or positive signal, respectively, maintaining the first order magnetic character of the phase transitions.

Figure 3 shows the deformation versus temperature curves, obtained from relation (15), for the same sets of parameters considered above. Note that for set 1, $\omega=\alpha T$, and we used for all numerical study the thermal expansion coefficient $\alpha=0.000017$ K^{-1}, which is the value for copper, see the dotted line in Fig. 3. There is not any particular interest in the adopted α value (and other copper parameters), and it is only considered here for numerical studies. The highest de-
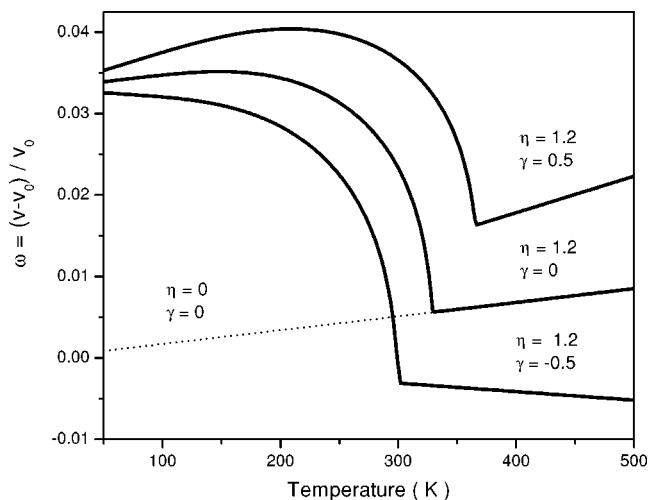

FIG. 3. Temperature dependence of the deformation for different model parameters sets considered in the text.

formation change, in the ordered ferromagnetic phase occurs for set 4 since these model parameters lead to the most abrupt order-disorder transition, as can be observed in Fig. 2. From relation (15), in the paramagnetic phase ($\sigma=0$) a critical $\gamma=\gamma_C=-\alpha V_0/3RK$ appears. For $\gamma > \gamma_C$ the deformation increases with the temperature and for $\gamma < \gamma_C$ the deformation decreases with temperature, i.e., the negative thermal expansion occurs. The sets 1–3 lead to normal deformations and set 4 leads to the negative thermal expansion, as shown in Fig. 3.

Figure 4 shows the curves of ΔS versus temperature for a magnetic field change from zero to 5 T. The highest peak in ΔS occurs for the parameters from set 4, as expected, since, as higher the derivative of magnetization with temperature is, higher is the change in the entropy with magnetic field change, as stated by the Maxwell relation. Comparison among the curve obtained with set 1 (dotted curves with second order transition), with the other curves, evidences the
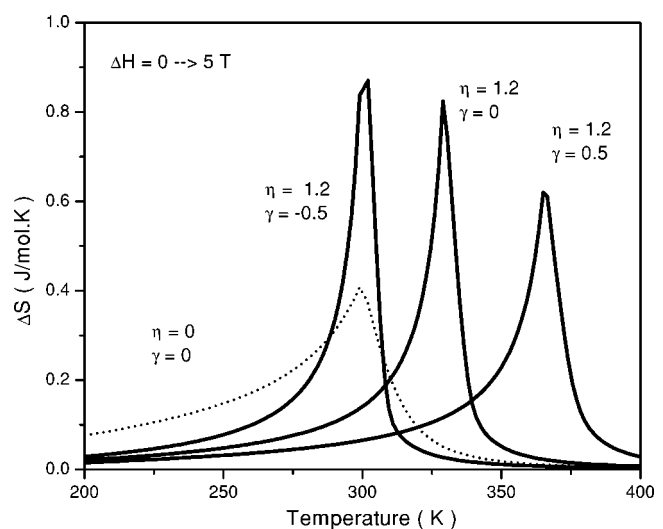

FIG. 4. Total entropy change versus temperature, for magnetic field changes from zero to 5 T, for different model parameters sets considered in the text.
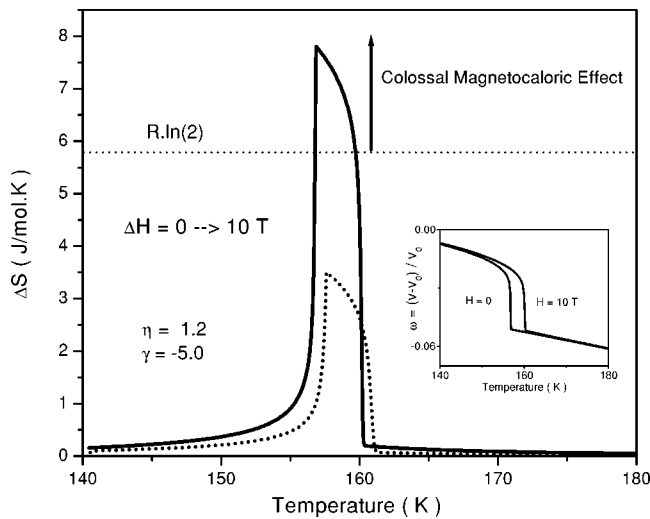
FIG. 5. Total entropy change versus temperature, for magnetic field changes from zero to 10 T, for model parameters from set 5. The inset shows the deformation versus temperature for $H=0$ and $H=10$ T.
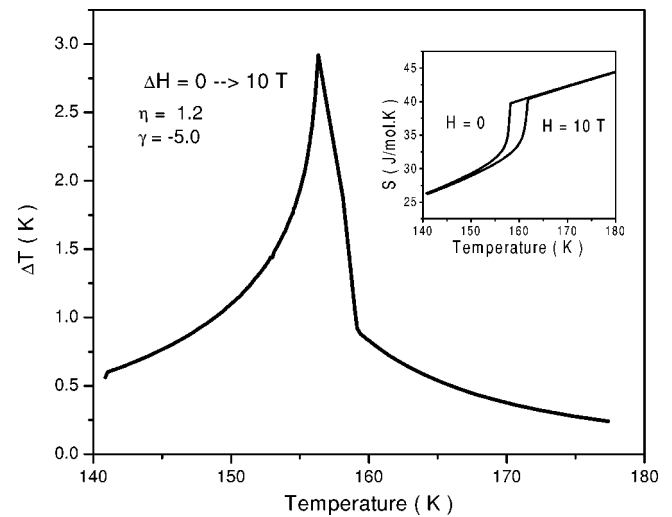

FIG. 6. Adiabatic temperature change versus temperature, for magnetic field changes from zero to 10 T, for model parameters from set 5. The inset shows the total entropy versus temperature for $H=0$ and $H=10$ T.

importance of the first order phase transition in attaining high magnetocaloric effect. Nevertheless, the area under the curves in Fig. 4 concentrates at Curie temperature when the ΔS peaks increase. This area is given here in Joule per mol units and represents the system cooling power, which is conserved within the numerical accuracy of our calculations (area ~ 22.7 J/mol for all curves). In practical interest, it is desired a high cooling power in as spread temperature range as possible, and an optimum composite refrigerant material can be simulated in order to achieve this goal, Refs. 15, 25, and 26.

In order to investigate the influence of the lattice entropy on the total entropy change, relation (17), the model parameters set 5 ($\eta=1.2$, $\gamma=-5.0$), and $\Theta=150$ K were considered for magnetic field change from zero to 10 T, see Fig. 5 solid curve. An outstanding result emerges, in which the peak value of ΔS exceeds the maximum magnetic entropy change, in our case $\Delta S_M^{\max}=R\ln(2J+1)=R\ln(2)\approx 5.76$ J/mol K. In a given material, when the maximum value of the entropic magnetocaloric effect exceeds the maximum magnetic entropy change, we called this effect the colossal magnetocaloric effect (CMCE). The origin of the CMCE in our model calculation comes from the lattice entropy. The inset of Fig. 5 shows ω versus temperature, for $H=0$ and $H=10$ T. As the temperature increases and reaches the Curie temperature, an abrupt decrease in ω occurs, as well as in the Debye temperature, see relation (10). When the Debye temperature decreases the lattice entropy increases. Since the external magnetic field increases the first order Curie temperature, a shift takes place in the ω vs T curve (see the inset of Fig. 5) and consequently occurs a shift in the temperature where the lattice entropy increases, which leads to the CMCE.

The ΔS vs T, dotted curve in Fig. 5, was calculated using the same parameters considered for the solid curve in Fig. 5, but not including the entropy change associated with the volumetric effect, relation (20), i.e., the dotted ΔS vs T curve was calculated using relation (7) which comes directly from

Maxwell relation (6) considering $V=$const. Comparison between these two curves shows that the volume change is responsible for approximately half of the total entropy change, for the considered model parameters.

Figure 6 shows the adiabatic temperature change vs temperature, see relation (19), obtained using the same parameters considered in the construction of the ΔS solid curve in Fig. 5. It is worth noticing that the maximum value $\Delta T^{\max}\approx 3$ K occurs around the Curie temperature. The colossal values in ΔS does not lead, necessarily, to high values in ΔT since, in our case, the shift in the total entropy change discontinuity due to the magnetic field change takes place in a narrow temperature window as displayed in the inset of Fig. 6. The temperature window appears since the magnetic field affects the transition temperature. This behavior usually occurs in materials which have first order magnetic phase transitions [e.g., the paramagnetic-ferromagnetic transition temperature in $Gd_5(Si_{1.72}Ge_{2.28})$ is linearly shifted from 250 to 300 K by an increasing magnetic field from zero to 10 T, Ref. 27].

FINAL COMMENTS

Using a simple model, the importance of the coupling between magnetic and crystal lattice in the study of the magnetocaloric effect was highlighted. Generally, the giant magnetocaloric materials present discontinuity in lattice parameters which can lead to large changes in cell volume and/or crystallographic structure at a critical first order magnetic phase transition temperature.[3,4,6] In our parametric study the deformation is very high, reaching values around $\omega=1,1\%$ (at the discontinuity transition temperature). It is not our aim, in this work, to fit a realistic material but only to investigate a model to deal with magnetocaloric materials which present high magnetoelastic effect. However, there are some magnetic systems that deserve to be investigated using the pro-

posed model. The linear thermal-expansion measurements, in the giant magnetocaloric material $Gd_5(Si_{1.8}Ge_{2.2})$, showed that a large volume contraction of $\omega=0.4\%$ takes place spontaneously at the first order magnetic transition temperature $T_C=240$ K (Ref. 28). The compound MnAs, for example, presents a ferromagnetic-paramagnetic first order phase transition, at about $T_C=310$ K, accompanied by giant volume change of about $\omega=2\%$ (Ref. 29). For these materials, very careful magnetocaloric investigations must be performed both from experimental and theoretical points of view. If the lattice is sensitive to the magnetic field, as considered in our CMLM study, the calculation of the magnetocaloric potential ΔS from the magnetic Gibbs energy must be done with care, being sure to take account the total entropy of the system. From the theoretical point of view, the model used to adjust the values of ΔS and ΔT must incorporate the relevant magnetic and lattice parameters, especially the temperature and magnetic field dependence of the structural lattice parameters, as recently investigated in the Gd_5Ge_4 system by Pechasky *et al.*[30]

The CMCE predicted in our theoretical model comes from the coupling between the crystalline and magnetic lattices and shows, quantitatively, the limitation of the ΔS calculation when one uses the Maxwell relation without taking account of the extra terms arising when the magnetoelastic effects are considered. A model to properly describe the entropy exchange between coupled magnetic and crystal lattices, in an adiabatic magnetic field change and in first order magnetic-volumetric transition process, is of fundamental importance to understand and improve giant magnetocaloric materials.[31] Our analytical CMLM contemplates, in a simple way, the existence of CMCE.

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