



# Effects of the temperature dependence of the bulk modulus on magnetic exchange-entropy



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## ABSTRACT

We have studied the field-induced additional exchange-entropy on an elastic ferromagnet as a response effect of the dependence of its bulk modulus with temperature. We consider that the temperature dependence of the bulk modulus follows a linear behavior or a Wachtman-type equation. Our analysis is based on a free energy model containing exchange, Zeeman and elastic terms. From the deduced expressions for the exchange parameter, the additional exchange-entropy was obtained. This quantity must be the difference between the conventional and the total entropy change which were calculated from well-established thermodynamic expressions, i.e., configurational spin disorder and Maxwell's equation, respectively. In addition, we established an analytical relation between the field-induced additional exchange-entropy and the temperature dependence of the bulk modulus.

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## 1. Introduction

The magnetoelastic behavior of some magnetic materials is of fundamental interest to both the point of view of basic physics and applications. Particularly, it is an important topic for the development of refrigeration technology at room temperature, which is one of the applications of the magnetocaloric effect (MCE) [1,2].

This topic has received renewed attention since the discovery in 1997 of giant MCE (compared to Gd prototype refrigerant) in the  $Gd_5Ge_2Si_2$  compound [3]. Among the materials with adequate performance to be used as refrigerant there are some that present strong magnetoelastic coupling. However, this kind of coupling can induce thermal and magnetic hysteresis, at a first order phase transition, which is responsible for making magnetic refrigerants less efficient in a refrigeration cycle. A reduced hysteresis, as well as large isothermal entropy change over a broad range of temperatures, is desirable for the magnetic refrigeration technology. In fact, the necessity of hysteresis loss reduction in  $Gd_5Ge_2Si_2$  has been emphasized since 2004 as a problem to be solved [4].

The thermodynamic framework for magnetoelastic coupling in the very interesting MnAs ferromagnetic compound goes back to the classic work of Bean and Rodbell in 1962 [5]. This material exhibits large hysteresis and a giant MCE at the transition temperature of 313 K that is accompanied by a simultaneous structural

transition. In this case, around the Curie temperature, it is observed a first-order transition between a ferromagnetic hexagonal phase to a paramagnetic orthorhombic phase [6].

As pointed out recently [7], the ferromagnetic mode of MnAs is kept for a slight doping with Cr which reduces, or even eliminates, the large thermal hysteresis of MnAs, but decreases the transition temperature. As instance,  $T_C = 267$  K for  $x = 0.001$  in  $Mn_{1-x}Cr_xAs$ .

First-order phase transitions are characterized by the coexistence of phases and can lead to a large change in volume in a short interval of temperature. There is a simultaneous possibility of a change in elastic constants across the transition region [8]. It suggests that the elastic term of the free energy must be conveniently analyzed to evaluate the magnetic and thermal behavior across the transition between the two phases. In this respect, it is interesting to study the entropy change of a material when subjected to an external mechanical action which is known as the mechanocaloric effect, i.e. the thermal response to uniaxial stress (elastocaloric) or to hydrostatic pressure (barocaloric), which is largest near structural phase transitions [9–11]. In the present work, however, we discuss only the magnetocaloric effect.

In a previous paper, some of the authors of the current work have reported a contribution to magnetic entropy for elastic ferromagnets called additional exchange-entropy [12]. When it is added to the conventional second-order field-induced entropy change, we recover the total entropy change obtained from the Maxwell's relation that involves derivatives of magnetization with respect to temperature. This model was later applied to the  $Gd_5Ge_2Si_2$

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and MnAs<sub>0.95</sub>Sb<sub>0.05</sub> compounds [13]. In both cases, the main contributions to entropy change are exchange and magnetoelastic energy terms [14]. The last one is mainly due to an indirect role to the MCE through modifications in the volume and consequently in the exchange parameter. The temperature and field dependence of the exchange parameter were deduced in a phenomenological way. In the present study, based on a free energy model containing exchange, Zeeman and elastic terms, we consider that the temperature dependence of bulk modulus follows a linear behavior or a Wachtman type equation [15]. Then, it is possible to obtain the temperature and field dependence of the exchange parameter from the free energy in a direct way. Analytical expressions for deformation as well as the additional entropy are obtained and the temperature and field behavior of exchange parameters are shown. Our results demonstrate the validity of the field-induced additional exchange-entropy and provide further support to the adequacy of the model.

## 2. Theory

In the mean field theory, the equation of state for rigid ferromagnets can be functionally defined by the Brillouin function,  $B_J(x)$ , with argument  $x = g\mu_B(H + H_{mol})/k_B T$ , through:

$$M = NgJ\mu_B B_J(x) \quad (1)$$

The molecular field being  $H_{mol} = \eta M$  and the spin configurational entropy given by:

$$S_{con} = R \int x \frac{\partial B_J(x)}{\partial x} dx \quad (2)$$

Eq. (2) is used to obtain the conventional field-induced magnetic entropy change at each temperature:

$$\Delta S_{con} = S_{con}(H_{final}) - S_{con}(H_{initial}) \quad (3)$$

When calculating the magnetic properties using an exchange parameter which depends on the volume strain,  $\eta(\omega)$ , one can build the free Gibbs energy [5], per volume unity, by means of exchange, Zeeman and elastic term

$$G(M, \omega) = -\frac{1}{2}\eta M^2 - HM + \frac{B\omega^2}{2} - TS \quad (4)$$

where  $\eta = \eta_0(1 + \beta\omega)$  is the exchange parameter being  $\beta$  a constant,  $B$  is the bulk modulus (inverse of the compressibility,  $K$ ) and  $S$  is the entropy. Note that the supposed exponential decay or growth of the exchange parameter with distance is expanded up to first order in deformation.

From minimizing the free energy in relation to relative deformation,  $\frac{\partial G(M, \omega)}{\partial \omega} = 0$ , one obtain:

$$\omega(M) = \frac{1}{2}K\eta_0\beta M^2 \quad (5)$$

Substituting Eq. (5) into Eq. (4), results:

$$G(M, \omega) = -\frac{1}{2}\eta^* M - HM - TS \quad (6)$$

where  $\eta^* \equiv \eta_0(1 + \beta\omega/2)$ . Thus, the elastic term can be absorbed by the exchange one. This is also the situation in the case that there are more contributions to the free energy. In this respect, for any  $\eta(H, T)$  dependence, it has been derived a field-induced additional exchange-entropy change [12] given by:

$$dS_{add}(H, T) = M \left( \frac{\partial \eta}{\partial T} \frac{\partial M}{\partial H} - \frac{\partial \eta}{\partial H} \frac{\partial M}{\partial T} \right) dH \quad (7)$$

in such a way that total entropy-change satisfies:

$$\Delta S_{Maxwell} = \Delta S_{con} + \Delta S_{add} \quad (8)$$

The left side in Eq. (8) can be calculated from magnetization curves, using the well-known Maxwell's relation, as:

$$\Delta S_{Maxwell}(T)_{\Delta H} = \int_{H_{initial}}^{H_{final}} (\partial M / \partial T)_H dH \quad (9)$$

which is valid for a system in thermodynamic equilibrium.

## 3. Results and discussion

If the relative deformation (or the exchange parameter) is a unique function of  $M$ , for instance having the quadratic form in Eq. (5), then Eq. (7) has a null contribution and  $\Delta S_{con}$  is the only contribution to the total entropy change. This is also the case when a type of anharmonic term is included in the free energy [16].

To obtain the case  $\Delta S_{add} \neq 0$ , we consider the bulk modulus dependence with temperature in the elastic term of Eq. (4). Such dependence has been reported recently for different systems by a number of authors, see, e.g., Refs. [17,18]. For simplicity, in this study, we consider a linear and a Wachtman-type dependence of the bulk modulus with the temperature [19]. They are written as:

$$B(T) = B_0[1 - b(T - a)] \quad (10)$$

and

$$B(T) = B_0 - a \text{Tex}p(-b/T) \quad (11)$$

for the linear case (L-case) and Wachtman case (W-case), respectively. Here,  $a$  and  $b$  are constants and  $B_0$  is the modulus value at a reference temperature, i.e.,  $T = a$  for the L-case and  $T = 0$  in the W-case. Minimizing the free energy in relation to the deformation, we obtain:

$$\omega(M, T) = \frac{1}{2B(T)}\eta_0\beta M^2 \quad (12)$$

From relation (12), we observe the  $M^2$  dependence together with an explicit temperature contribution for the deformation through the bulk modulus.

Using  $\eta = \eta_0(1 + \beta\omega)$  and Eqs. (10)–(12), one can obtain from Eq. (7), the differential form of the additional entropy change:

$$dS_{add}(H, T) = \frac{b}{2B_0[1 - b(T - a)]^2}\eta_0^2\beta^2 M^3 \frac{\partial M}{\partial H} dH \quad (13)$$

and

$$dS_{add}(H, T) = \frac{(1 + b/T)\text{exp}(-b/T)}{2[B_0 - a \text{Tex}p(-b/T)]^2} a \eta_0^2 \beta^2 M^3 \frac{\partial M}{\partial H} dH \quad (14)$$

for the L-case and W-case, respectively. From Eqs. (13) and (14) it follows  $\Delta S_{add} = 0$  if the bulk modulus is a constant, i.e.,  $a = 0$  ( $b = 0$ ) in the W-case (L-case).

To perform the numerical calculations we have chosen  $g = 2$ ,  $J = 3/2$ ,  $\beta = 10$ ,  $B_0 = 4.52 \times 10^5$  (J/mol) and  $\eta_0 = 1466$  (T<sup>2</sup>/meV), similar data set as that used for the MnAs compound [5]. For the L-case, the additional parameters  $a = 300$  (K) and  $b = 2 \times 10^{-3}$  (K<sup>-1</sup>) were used. For the W-case the chosen parameters were  $a = 790$  (J/mol K) and  $b = 300$  (K). These sets of parameters reproduce the relative volume change of the order of that observed in MnAs around the transition. Magnetization was calculated from Eq. (1) where the argument is obtained from  $(\partial G / \partial M) / (k_B T)$ . The results, for fields between 2 and 5 T, are showed in Fig. 1(a) and (b) where it is observed a smooth and a more abrupt behavior of  $M$  vs.  $T$  for the L and W cases, respectively. The reason to use this interval of fields is to guarantee differentiable curves  $M(H, T)$  and  $\eta(H, T)$ . This last is obtained using  $\eta = \eta_0(1 + \beta\omega)$  and Eq. (12).

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