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Colossal magnetocaloric effect in magneto-auxetic systems

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Abstract

We show that a mechanically driven magnetocaloric effect (MCE) in magneto-auxetic systems (MASs) in the vicinity of room temperature is possible and the effect can be colossal. Even at zero external magnetic field, the magnetic entropy change in this reversible process can be a few times larger in magnitude than in the case of the giant MCE discovered by Pecharsky and Gschneidner in $Gd_5(Si_2Ge_2)$. MAS represent a novel class of metamaterials having magnetic insertions embedded within a non-magnetic matrix which exhibits a negative Poisson's ratio. The auxetic behaviour of the non-magnetic matrix may either enhance the magnetic ordering process or it may result in a transition to the disordered phase. In the MAS under consideration, a spin 1/2 system is chosen for the magnetic component and the well-known Onsager solution for the two-dimensional square lattice Ising model at zero external magnetic field is used to show that the isothermal change in magnetic entropy accompanying the auxetic behaviour can take a large value at room temperature. The practical importance of our findings is that MCE materials used in present engineering applications may be further enhanced by changing their geometry such that they exhibit auxetic behaviour.

Keywords: magnetocaloric effect, auxetic system, phase transition

(Some figures may appear in colour only in the online journal)

1. Introduction

The magnetocaloric effect (MCE) is a phenomenon related to the heating of a magnetic material upon the application of a magnetic field, and conversely, its cooling after the removal of a magnetic field. MCE was first discovered in iron by Warburg in 1881 [1] and since then, a vast number of studies have been carried out on this phenomenon [2, 3]. MCE is an intrinsic property of magnetic materials but it is usually too weak to be used in everyday magnetic cooling applications operating at around room temperature. Exceptions to this are gadolinium (Gd), which has a critical temperature of T_c = 294 K, various compounds based on manganites, and related compounds of rare earth metals [3]. Significant progress concerning new MCE materials has been noted since the discovery of giant MCE in $Gd_5(Si_2Ge_2)$ by Pecharsky and Gschneidner [4]. In this study, we show how magneto-auxetic systems (MASs), systems which exhibit auxetic behaviour, can also demonstrate an MCE.

Auxetic [5] materials exhibit a negative Poisson's ratio [6], that is they expand laterally when uniaxially stretched. The first papers on auxetic materials and structures appeared more than 20 years ago [5, 7–10] however only recently were they studied for their magnetic properties. Such studies include investigations on the magnetic properties of auxetic foams [11, 12], magnetic ferrogels [13, 14], $CoFe_2O_4$

epitaxial thin films [15], magnetostrictive iron–gallium alloys galfenol [16] and MASs [17]. Wave propagation was also investigated in magneto-elastic lattices [18].

MAS are systems which have magnetic insertions embedded within a non-magnetic auxetic matrix such that an external magnetic field can control both their mechanical and magnetic properties [17]. In this study, we suggest the possibility of achieving a large mechanically driven MCE at around room temperature by using an MAS. These systems can also exhibit MCE at zero external magnetic field. In such a case, the mechanical deformation of MAS subjected to external stresses couples the rotational and translational motion of its auxetic units and it becomes the counterpart of the application of an external magnetic field. In addition to a mechanical deformation, an application of an external magnetic field enhances the MCE proportionally to the strength of the magnetic field, as occurs in classical MCE materials.

It should be noted that the concept of MCE occurring at zero external magnetic field has already been introduced [3], as has the concept of mechanical deformations affecting the MCE [16, 19]. In particular, Tishin and Spichin introduced the concept of an elastocaloric effect which arises by changing the external pressure at a constant (or zero) magnetic field [3]. A study by Mosca *et al* showed that strain can tune MCE related to the magneto-structural phase transition in MnAs [19]. It was found that the critical temperature of the strained epilayers of MnAs depends on the mean strain ε as $T_c = T_0(1 + 2\kappa\varepsilon)$ for some adjustable parameters T_0 and κ. In a paper by Paes and Mosca, the effect of an applied mechanical stress on galfenol was discussed and it was shown that magnetostriction and magnetoelastic interactions can be responsible for auxeticity in galfenol [16]. Below, a simple theoretical model for a MAS is introduced to show that the mechanical deformation of such a system can generate colossal changes in magnetic entropy compared to classic MCE.

2. MCE in magneto-auxetics and discussion

In [17], a novel class of metamaterials having a permanent magnetic insertion embedded within a non-magnetic auxetic matrix was introduced. The matrix was made up from $N_x \times N_y$ perfectly rigid rotating rectangles of dimensions $a \times b$ connected at their vertices by means of hinges [20]. The magnetic insertion was represented by a finite set of magnetic dipoles. To prove the possibility of emergence of the MCE in MAS around room temperature, the two-dimensional magneto-mechanical model [17] is converted into a microscopic spin 1/2 system which can exhibit phase transitions. For the sake of simplicity, $a = b$ (squares) and $N_x = N_y = N$ is chosen. Magnetic moments are represented by Ising spins $s_{ij} = \pm 1$ which are located at the centre of mass $\vec{r_{ij}}$ of the squares (i, j) where $i, j = 1, 2, \ldots, N$. A schematic representation of a MAS consisting of 3×3 square units is presented in figure 1. The centres of mass of the squares

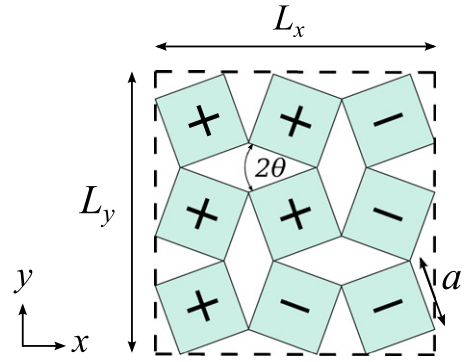

Figure 1. Magneto-auxetic system of 3×3 squares of dimension $a \times a$ with the exemplary configuration of Ising spins $s = \pm 1$ denoted by '+' and '−' respectively, located at center of mass of the squares. L_x and L_y denote linear size of the system in the x and y directions respectively.

create a two-dimensional square lattice where $L_x = L_y = L = \mathrm{N}a[\cos(\theta) + \sin(\theta)]$.

The nearest-neighbour Ising model Hamiltonian [21] is used to describe magnetic interactions as follows:

$$H_{\mathrm{exact}}^{\mathrm{IM}} = -\sum_{\langle ij,kl\rangle} J_{ij,kl} s_{ij} s_{kl} - \mu_{\mathrm{B}} H \sum_{i,j=1}^{N} s_{ij}, \tag{1}$$

where the angular brackets denote summation over the nearest-neighbour lattice pairs, H is the external magnetic field measured in Teslas, μ_{B} is the Bohr magneton, $J_{ij,kl}$ is the exchange integral which depends on the distance $r_{ij,kl}$ between the nearest-neighbour sites (i, j) and (k, l). It is assumed that $J_{ij,kl} = J_0 / r_{ij,kl}^3$ and $J_0 > 0$ (ferromagnetic interaction). For the squares as in figure 1, the distance $r_{ij,kl} = a\sqrt{2}\sin\left(\theta + \frac{\pi}{4}\right)$. The auxetic deformation does not change the symmetry of the magnetic Hamiltonian because the centres of mass of the rotating squares are represented by a square lattice for any value of θ.

In a closed thermodynamic system of localized magnetic moments, the total entropy S depends on the temperature T, pressure p, and external magnetic field H. The full differential of the entropy can be written as:

$$\mathrm{d}S = \left(\frac{\partial S}{\partial T}\right)_{p,H} \mathrm{d}T + \left(\frac{\partial S}{\partial p}\right)_{T,H} \mathrm{d}p + \left(\frac{\partial S}{\partial H}\right)_{T,p} \mathrm{d}H. \tag{2}$$

The MCE phenomenon is represented by the isobaric-isothermal process ($\mathrm{d}p = 0$, $\mathrm{d}T = 0$) where:

$$\mathrm{d}S = \left(\frac{\partial S}{\partial H}\right)_{T,p} \mathrm{d}H \tag{3}$$

and usually it can be expressed in two ways:

(i) by the temperature increase $\Delta T = T_f - T_i > 0$ of the magnetic material after a change in the magnetic field $\Delta H = H_f - H_i > 0$, from the initial value H_i to the final value H_f, which is applied adiabatically through a thermodynamically reversible process,

(ii) by the decrease of the magnetic part S_M of the total entropy S after the magnetic field H_f ($H_f > H_i$) is applied

isothermally at temperature T, that is

$$\Delta S_M = S_M\left(T, H_f\right) - S_M\left(T, H_i\right) < 0. \tag{4}$$

There is another possibility of obtaining an entropy change equation (2) and this occurs through the isothermal process at constant magnetic field ($\mathrm{d}T = 0$, $\mathrm{d}H = 0$)

$$\mathrm{d}S = \left(\frac{\partial S}{\partial p}\right)_{T,H} \mathrm{d}p. \tag{5}$$

The elastocaloric effect [3] is an example of such a process. In MAS, the infinitesimally small uniaxial stress $\mathrm{d}\sigma_i$ for loading in the direction i (e.g. x or y) substitutes the infinitesimally small isotropic pressure change $\mathrm{d}p$ in equation (5). The stress $\mathrm{d}\sigma_i$ can be expressed in terms of Young's modulus E_i and the strain ε_i for loading in the direction i, i.e., $\mathrm{d}\sigma_i = E_i \mathrm{d}\varepsilon_i$. In the particular case of figure 1, $\mathrm{d}\varepsilon_i$ is equal for loading in the x and y direction, $\mathrm{d}\varepsilon_i = \frac{\mathrm{d}L_x}{L_x} = \frac{\mathrm{d}L_y}{L_y} = \frac{\mathrm{d}L}{L}$ where $\mathrm{d}L = a\,[\cos(\theta) - \sin(\theta)]\mathrm{d}\theta$. The full differential of the entropy from equation (5) can thus be expressed as:

$$\mathrm{d}S = \left(\frac{\partial S}{\partial \theta}\right)_{T,H} \mathrm{d}\theta. \tag{6}$$

A more general process is possible whereby the external magnetic field is changed from the initial field H_i to the final field $H_f\,(H_i < H_f)$ concurrent to an applied strain. In this case, the entropy decrease ΔS_M by the MCE during the isothermal process is given by:

$$\Delta S_M = S_M\left(T, H_f, \theta_f\right) - S_M\left(T, H_i, \theta_i\right) < 0, \tag{7}$$

where θ_i and θ_f represent the initial and final values of θ for which the distance between the magnetic moments decreases.

To be close to the experimental values concerning materials with an MCE near room temperature [3], the value of J_0 in the Hamiltonian of equation (1) is chosen to be equal to 0.01116 eV. This value is such that $T_\mathrm{c} = 293.9$ K for $\theta = 90°$ and $T_\mathrm{c} = 103.9$ K for $\theta = 45°$. The magnetic entropy isothermal change ΔS_M after the deformation $\Delta\theta = \theta_f - \theta_i$ can be easily determined with the help of the well-known Onsager solution [22–24] for the two-dimensional square lattice Ising model at zero magnetic field ($H = 0$). The entropy per site $s_M = S_M/k_\mathrm{B}$ is calculated as $s_M = \beta\,(\epsilon - F\,(T, 0))$. For the Ising model, the magnetic energy per site $\epsilon = -\frac{\partial f}{\partial \beta}$ and the free energy per site reduced by temperature $f = \beta F\,(T, 0)$ can be found [23]. It must be noted that the rotating squares system is used in order to have the exact Onsager solution for the Ising model, however there are other rotating rigid units systems which can be effectively used as a non-magnetic matrix.

In figure 2, the dependence of $\Delta s_M = \Delta S_M/k_\mathrm{B}$ per site on temperature is shown for different values of θ_i and θ_f with no external magnetic field present. The characteristic feature of the plotted magnetic entropy difference Δs_M is that its full width at half maximum is determined by the difference $\Delta T = T_\mathrm{c}(\theta_f) - T_\mathrm{c}(\theta_i)$ of the critical temperatures for the deformation $\Delta\theta = \theta_f - \theta_i$. In the model, $T_\mathrm{c} = T_\mathrm{c}^{\mathrm{sq}}\Big/\left(a\sqrt{2}\,\sin(\theta + \frac{\pi}{4})\right)^3$ where $T_\mathrm{c}^{\mathrm{sq}}$ is the critical temperature for the square lattice Ising model with the unit lattice constant and it includes magneto-volume coupling through the deformation parameter θ. Hence, there is a direct analogy with the dependence of the critical temperature on strain [19] and on the lattice volume as in the Bean–Rodbell model [25].

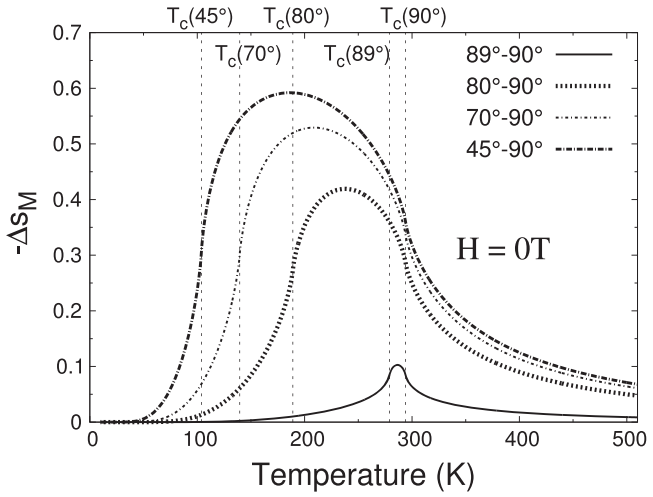

Figure 2. Temperature dependence of the isothermal entropy change Δs_M for MAS deformed from θ_i to θ_f at zero magnetic field. The plots representing deformations 89° → 90°, 80° → 90°, 70° → 90°, 45° → 90° are shown (units in degrees). The vertical lines indicate location of T_c for a given value of θ_i and θ_f.

In the case of a spin 1/2 model being taken into consideration, the maximum value of the reduced magnetic entropy $-\Delta s_M$ cannot exceed the value of $\log(2) \approx 0.693$ as for the Ising model. In figure 2, the largest value of the change in magnetic entropy is observed for the deformation from $\theta_i = 45°$ to $\theta_f = 90°$ where it is about 85% of the maximum possible value. The deformation of 1° from $\theta_i = 89°$ to $\theta_f = 90°$ (or equivalently from $\theta_i = 1°$ to $\theta_f = 0°$) corresponds to a $\Delta s_M \approx 15\%$ of the maximum entropy.

If Gd atoms (where the total angular momentum of an atom $J = 7/2$) are substituted for the Ising atoms, then, the maximum change in the magnetic entropy cannot exceed the value of $\log(8) \approx 2.079$. After multiplication with the gas constant for Gd atoms, this maximum value would correspond to 17.3 J mol^{-1} K or 110.02 J kg^{-1} K [3]. In this case, the entropy change by 15% of the maximum entropy value would result in 16.50 J kg^{-1} K. This latter value is more than three times larger than the maximum entropy change for Gd after an application of a magnetic field of 2 T (H_i = 0 T, H_f = 2 T) and it is of the same order of magnitude as in $Gd_5(Si_2Ge_2)$ for the same parameters (refer to figure 4 in the paper by Pecharsky and Gschneidner [4]).

The question arises whether such magnetic materials as in figure 1 exist in nature or not. The linear size L of such a system can increase up to 41% under a uniaxial strain applied in the x or y direction and an increase in area of up to 100%. In one of the three-dimensional versions of this auxetic system, its volume can increase by up to ≈180%. This can be compared to present MCE materials where often only a small

volume expansion $\Delta V/V < 0.1\%$ is observed at T_c due to a magnetoelastic transition. In some MCE materials, such as the intermetallic compound MnAs, which has a first-order phase transition, the volume expansion can be of the order of 2% [26]. A volume decrease of about 8% is observed in the phase transition of samarium from fcc to dhcp after an application of a pressure of 7×10^8 Pa at room temperature [3]. Comparing the volume changes of MCE materials with that of the model illustrated in figure 1 suggests that this model cannot be used to represent current MCE materials but is a new concept of how MCE can be achieved.

The strain driven, giant and reversible MCE in $La_{0.7}Ca_{0.3}MnO_3$ epitaxial ferromagnetic films [27] shows that the use of new MCE materials, instead of tuning existing magnetic materials, is nowadays common in the investigation of MCE. Recent discussion on magnetocaloric and electrocaloric effect by Moya *et al* can be found in [28]. The studies on nanoscale lanthanides and their alloys [29], as well as on ferrite nanoparticles [30] which represent a competitive alternative to conventional bulk MCE materials also show this current trend. In particular, single-domain magnetic nanoparticles are promising because of their superparamagnetic property above the blocking temperature T_b, their large area for heat exchange, as well as the possibility of placing them into another host material which material can be non-magnetic. Each magnetic nanoparticle acts as a single superspin which can interact with the surrounding superspins through dipolar interactions [31]. In the relatively dense ensemble of magnetic nanoparticles they can show collective behaviour typical of spin-glass or superferromagnetic systems [31–34]. In particular, in [31] the thin layers of $Co_{80}Fe_{20}$ nanoparticles which are embedded in a diamagnetic Al_2O_3 matrix were investigated and when the nominal thickness of the nanoparticles concentration exceeded the value of 1.1 nm, superferromagnetic ordering was observed with the magnetic domain structure of the nanoparticles' magnetic moments analogous to that observed in ferromagnets.

In fact, if one were to substitute the Ising spins found at the nodes of the lattice system being considered in the MAS model with the magnetic moments of single-domain magnetic nanoparticles of Fe_3O_4, one can show the extent of MCE. The magnetic moment per f.u. of the compound Fe_3O_4 is equal to $\mu/\text{f.u.} = 4.33\mu_B$ [35]. Then, if for example the magnetic nanoparticles are considered to have a dimension of 5 nm, the magnetic moment of nanoparticle can be estimated as $\mu \approx 3831\mu_B$. Moreover, if the centre-to-centre distance between two adjacent magnetic moments (or superspins as they were termed in [31]) is defined as d then, the potential energy of the superspin–superspin interaction can be determined as a function of d. Thus, assuming that $d = 5$ nm (i.e. the nanoparticles are touching each other) the ineraction potential energy is of $E/k_B \approx 73$ K. If we were to consider the four-nearest-neighbours interaction approach (that is the given superspin interacts with its four nearest neighbours) for $d = 5$ nm the total value of dipolar interaction energy is equal to $E/k_B \approx 293$ K. On the other hand, if the distance is of $d = 10$ nm the value of the energy including the four-nearest-neighbours interaction drastically decreases to $E/k_B \approx 37$ K. This result clearly indicates that a change in energy is occuring on changing the distance between the magnetic nanoparticles and it can be significant at room temperature. Similarly magnetic nanoparticles embedded within an MAS will undergo a change in their separation distance when a strain is applied to the system. This clearly indicates the extent of the MCE which arises when modifying the geometry of the system.

It has been confirmed experimentally that magnetic nanoparticles can be higly concentrated in a non-magnetic host matrix, even for small dimensions. In particular, iron oxide nanoparticles with an average diameter of 2–2.5 nm synthesized in mesoporous silica MCM-41 and MSS by means of a co-precipitation method were recently obtained experimentally [36].

3. Conclusions

It has been shown that a colossal MCE, which may occur around room temperature, is an intrinsic property of magneto-auxetic systems. This MCE can be driven by a mechanical strain at zero external magnetic field. On applying an external magnetic field, this MCE is further enhanced. This new concept of MCE can be of importance especially in applications where a large magnetic field cannot be used. Apart from this, the MCE proposed here can also be obtained from relatively cheap materials and thus increasing viability and practicality of technologies which make use of MCE. Due to the versatility of this MCE concept, it can be used in refrigeration technologies ranging from low temperatures to room temperatures and in coolers for nano and microelectromechanical devices.

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