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The anisotropic magnetocaloric effect described by Maxwell formulation: Application to $DyAl_2$ and $TbNi_2$

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In this work we present the Maxwell-like formulation of the anisotropic magnetocaloric effect for materials in single crystalline form subjected to a rotating applied magnetic field of constant intensity. This effect is a new topic in the magnetocaloric research area and can highlight some relevant mechanisms on spin reorientation. Application of the model to the ferromagnetic compounds $DyAl_2$ and $TbNi_2$, which are subjected to cubic crystalline electric field anisotropy and isotropic exchange interaction, are performed. We obtain continuous and discontinuous reorientation transitions for the Cartesian components of magnetization which revealed some characteristics of the anisotropic magnetocaloric curves.

1. Introduction

In the last twelve years the study of the magnetocaloric effect (MCE) has been stimulated by the discovery of the excellent magnetothermal properties in the $Gd_5(Si_xGe_{1-x})_4$ compounds [1,2] which was pointed out as potential candidates to be used as refrigerant materials. The MCE materials for magnetic refrigeration can be characterized by the adiabatic variation of temperature, ΔT, of a magnetic material upon changes in the intensity of the applied magnetic field, ΔH. In complement, this conventional MCE can be characterized by the magnetic field-induced change in entropy in an isothermal process, ΔS, for a given *magnetic field intensity change*. On the other hand, in the anisotropic magnetic materials, where the magnetization is dependent on the applied magnetic field orientation (in the crystallographic referential frame of the sample), two directions are particularly interesting: the easy magnetic direction and hard magnetic direction where the magnetization presents maximum and minimum values, respectively. The easy magnetic direction can be temperature and magnetic field dependent as is the case of the ferromagnetic $HoAl_2$ compound ($T_C = 30\,K$) which presents rotation from the [1 1 0] easy magnetic direction to the [1 0 0] one (at $T = 20\,K$) when the magnetic field applied along [1 0 0] direction reaches the critical values of 0.1 T [3,4]. Evidently, under these conditions, one can expect a change in the magnetic entropy due to the field-induced spin reorientation process. Therefore, in anisotropic magnetic materials the magnetization dependence on the magnetic field direction can lead to a strong dependence of the magnetic entropy on the relative orientation of the applied magnetic field, *i.e.*, for a fixed magnetic field intensity the entropy can change upon *magnetic field direction change*. In this way, for anisotropic materials, both ΔS and ΔT should be properly investigated maintaining constant the intensity of the applied magnetic field and changing its direction (in relation to crystallographic axes).

Anisotropic entropy changes in magnetic systems are of particular interest for the magnetocaloric effect due to the possibility to explore the spin reorientation process [5]. Among the magnetic systems that present field-induced spin reorientation are some lanthanide-based compounds due to the existence of the magnetic anisotropy that comes from the crystalline electric field (CEF) [6,7].

In this work we report a study about the determination of the entropy changes in systems subject to cubic CEF and isotropic exchange interactions under the influence of changing the magnetic field direction. Additionally, we extend the Maxwell's thermodynamic relation used in the conventional MCE (where the magnetic field intensity changes at fixed magnetic field direction)

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to obtain the ΔS in anisotropic version (where the magnetic field direction changes for fixed magnetic field intensity). Applications of the model were performed in $DyAl_2$ and $TbNi_2$ compounds.

2. Theory

The measures and conventional calculations of the magnetic entropy change upon magnetic field intensity change (from H_i to H_f) can be obtained from magnetization data through the well-known integral which follows from the differential Maxwell's relation [8].

$$\Delta S(T) = \int_{H_i}^{H_f} \left(\frac{\partial M}{\partial T} \right) \, dH \tag{1}$$

On the other hand, the isothermal and adiabatic anisotropic-MCE potentials were introduced in a recent work by von Ranke et al. [9]. To do this it was necessary to define the set (α_e, β_e, γ_e) which describes the angles formed between the applied magnetic-field vector (in the easy magnetic direction) and the Cartesian axes x, y, and z, respectively. The set (α, β, γ) similarly describes the angles formed between the applied magnetic-field vector when in an arbitrary direction in relation to the Cartesian axes and the anisotropic entropy change is defined as the difference between $S\,(T, H, \alpha_e, \beta_e, \gamma_e)$ and $S\,(T, H, \alpha, \beta, \gamma)$.

One can extend this definition by considering arbitrary directions for the applied magnetic field. Therefore, in order to obtain the Maxwell-like formulation for the anisotropic isothermal magnetocaloric potential, we consider an arbitrary orientation for the magnetic field in relation to the magnetization vector. In this way, the Maxwell's relation leads to the following isothermal entropy change:

$$dS = \frac{\partial \vec{M}}{\partial T} \cdot d\vec{H} \tag{2}$$

For the investigation of the above entropy change, $d\vec{H}$ is obtained fixing the field intensity and changing its direction. In spherical coordinate system, an infinitesimal change in $\vec{H}$ from one arbitrary direction (θ, ϕ) to another direction ($\theta + d\theta$, $\phi + d\phi$) is given by:

$$d\vec{H} = H \left[\left(\frac{\partial \hat{u}(\theta, \phi)}{\partial \theta} \right)_{\phi} d\theta + \left(\frac{\partial \hat{u}(\theta, \phi)}{\partial \phi} \right)_{\theta} d\phi \right] \tag{3}$$

where $\hat{u}(\theta, \phi)$ is the unit vector parallel to $\vec{H}$. The infinitesimal change $d\vec{H}$ can be written in terms of the fixed Cartesian unit vectors $\hat{x}$, $\hat{y}$ and $\hat{z}$ as:

$$\begin{aligned} d\vec{H} &= H[(\cos\theta \cos\phi \hat{x} + \cos\theta \sin\phi \hat{y} - \sin\theta \hat{z}) d\theta \\ &\quad + (-\sin\theta \sin\phi \hat{x} + \sin\theta \cos\phi \hat{y}) d\phi] \end{aligned} \tag{4}$$

From relations (2) and (4) the following entropy change, due to the magnetic field change direction, is obtained:

(i) for fixed azimuthal angle ϕ:

$$-\Delta S_{an}^{\theta_i \to \theta_f}(T) = H \int_{\theta_i}^{\theta_f} \left(\cos\theta \cos\phi \, \frac{\partial M_X}{\partial T} + \cos\theta \sin\phi \, \frac{\partial M_Y}{\partial T} - \sin\theta \, \frac{\partial M_Z}{\partial T} \right) d\theta \tag{5}$$

(ii) for fixed polar angle θ:

$$-\Delta S_{an}^{\phi_i \to \phi_f}(T) = H \int_{\phi_i}^{\phi_f} \left(-\sin\theta \sin\phi \, \frac{\partial M_X}{\partial T} + \sin\theta \cos\phi \, \frac{\partial M_Y}{\partial T} \right) d\phi \tag{6}$$

where M_X, M_Y and M_Z are the Cartesian components of the magnetization.

It is worth noticing that the anisotropic-MCE is related with the transversal component of the magnetization whereas the conventional MCE is related to the longitudinal component, *i.e.*, along the field direction. In fact, it is easy to show that relations (5) and (6) can be written as

$$-\Delta S_{an}^{\theta_i \to \theta_f}(T) = H \int_{\theta_i}^{\theta_f} \left(-\frac{\partial M_t^{\phi}}{\partial T} \right) d\theta, \tag{7}$$

and

$$-\Delta S_{an}^{\phi_i \to \phi_f}(T) = H \int_{\phi_i}^{\phi_f} \left(-\frac{\partial M_t^{\theta}}{\partial T} \right) d\phi, \tag{8}$$

where $M_t^{\phi} = \left(M_X \cos\theta \cos\phi + M_Y \cos\theta \sin\phi - M_Z \sin\theta \right)$ and $M_t^{\theta} = \left(-M_X \sin\theta \sin\phi + M_Y \sin\theta \cos\phi \right)$ are the transversal components of the magnetization corresponding to fixed ϕ and θ, respectively. Relations (7) and (8) are the Maxwell-like formulation for the anisotropic magnetocaloric effect.

On one hand, if the transversal magnetization components are obtained experimentally as function of temperature and for different directions of external magnetic field (either ϕ or θ constant), one can obtain $-\Delta S_{an}$ by means of relations (7) and (8). On the other hand, in order to calculate theoretically $-\Delta S_{an}$, for a rotation of the applied magnetic field from (θ_i, ϕ_i) to (θ_f, ϕ_f) in the system under study, one can determine the thermal behavior of the magnetization components which appear in relations (5) and (6). It is interesting to perform calculations for the case of rare earth magnetic compounds and we consider a Hamiltonian including the CEF, Zeeman and exchange interactions (in mean field approximation). From this Hamiltonian, the energy eigenvalues, ε_n, and eigenvectors, $|n\rangle$, are numerically determined to calculate the magnetization components. Details of the calculations of magnetization and entropy were described elsewhere [9]. In short, for a given magnetic field direction, one can use relations (9) and (10) to obtain the magnetization components $\alpha = (x, y, z)$ as well as the directional magnetic entropy of the magnetic system under investigation.

$$M_{\alpha}^{\vec{H}} = g\mu_B \frac{\sum_{n=1}^{2J+1} \left\langle n \left| \hat{J}_{\alpha} \right| n \right\rangle e^{-\varepsilon_n / k_B T}}{\sum_{n=1}^{2J+1} e^{-\varepsilon_n / k_B T}} \tag{9}$$

$$S^{\vec{H}} = R \left\{ \frac{1}{k_B T} \frac{\sum_{n=1}^{2J+1} \varepsilon_n e^{-\varepsilon_n / k_B T}}{\sum_{n=1}^{2J+1} e^{-\varepsilon_n / k_B T}} + \ln \sum_{n=1}^{2J+1} e^{-\varepsilon_n / k_B T} \right\} \tag{10}$$

In the following we will apply the above relations to study some aspects of the anisotropic-MCE in the ferromagnetic cubic compounds $DyAl_2$ and $TbNi_2$.

3. Application and discussion

The $DyAl_2$ compound has been extensively studied (Ref. [9], and references therein). The $DyAl_2$ presents cubic symmetry and orders ferromagnetically below 61 K with the easy axis along the [1 0 0] direction.

The cubic-crystalline axes are usually oriented parallel to the Cartesian ones, being z-[0 0 1] the orientation of the selected easy magnetic direction, chosen here as the quantization axis. In order to perform the calculations in the anisotropic $DyAl_2$ compound we used the same set of CEF and exchange parameters considered in Ref. [9]. The magnetization isotherms curves were calculated changing the magnetic field (of fixed intensity $H = 5$ T) from [0 0 1] to [1 1 1] direction, in a plane defined by these directions, *i.e.*, fixing the azimuthal angle at $\phi = \pi/4$ and varying the angle θ. Fig. 1(a) shows calculated results for the Cartesian components of magnetization in terms of the polar field-angle where one can note the

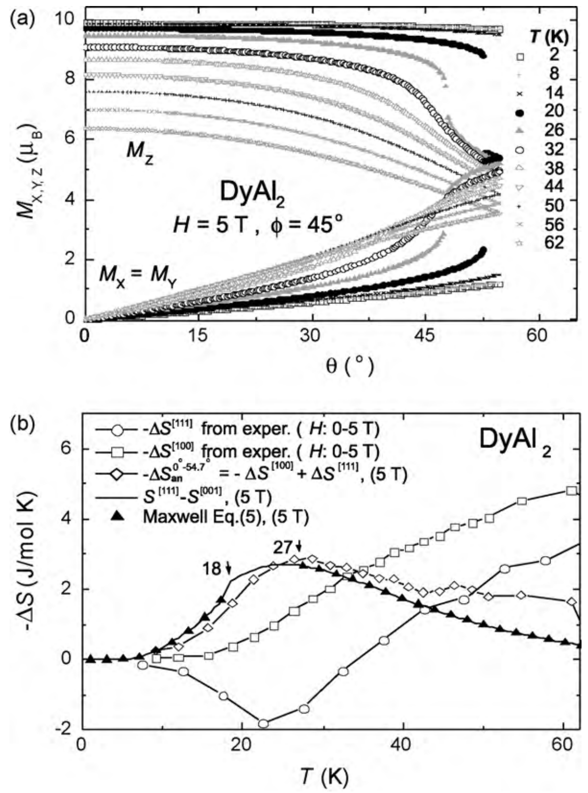

Fig. 1. (a) Calculated components of magnetization in DyAl$_2$ compound, $M_X = M_Y$ (lower curves) and M_Z (upper curves), in function of the polar field-angle for selected temperatures. (b) Deduced anisotropic entropy change from experimental conventional entropy changes at [1 0 0] and [1 1 1] directions (obtained from Ref. [6]). Theoretical results corresponds to direct calculations $S^{[1\,1\,1]} - S^{[0\,0\,1]}$ (solid line) and from Maxwell's relation (5) (solid triangles) for $H = 5$ T, $0^\circ \leq \theta \leq 54.7^\circ$ and $\phi = 45^\circ$.

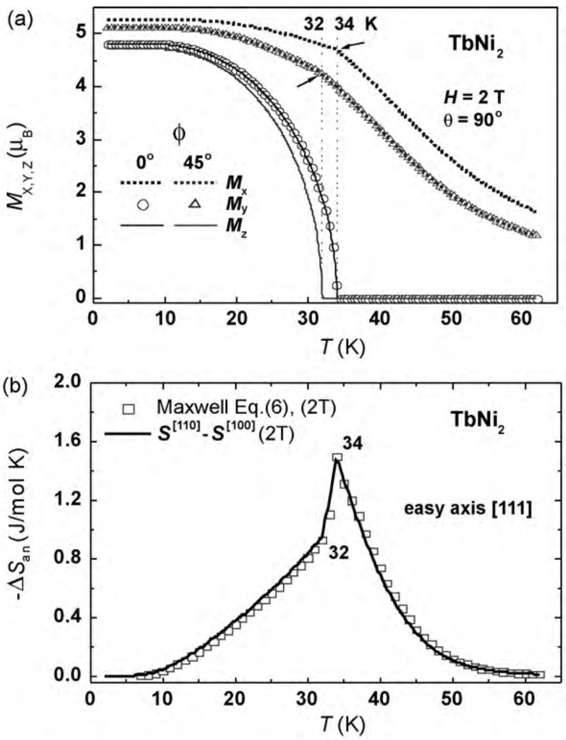

Fig. 2. (a) Calculated components of magnetization in TbNi$_2$ compound as a function of the temperature for selected azimuthal field-angles, $H = 2$ T and $\theta = 90^\circ$. (b) Theoretical calculations, $S^{[1\,1\,1]} - S^{[0\,0\,1]}$ (solid line) and from Maxwell's relation (6), (open squares) for $H = 2$ T, $0^\circ \leq \phi \leq 45^\circ$ and $\theta = 90^\circ$.

discontinuities for the temperature ranges from 18 to 27 K (approximately) due to the first order spin reorientations process. It is worth noticing the paramagnetic–metamagnetic-like behavior of the M_X and M_Y magnetization components (lower curves) and the ferromagnetic-like behavior of the M_Z component (upper curves). Due to the symmetry of the magnetic field rotation at fixed $\phi = 45^\circ$, we have $M_X = M_Y$ for $0^\circ \leq \theta \leq 54.7^\circ$ and all temperatures. Note that at low temperatures $M_X = M_Y \approx 0$ and $M_Z \approx 10\mu_B$ since the easy magnetic direction is [0 0 1]. As the temperature increases the component M_Z decreases and the components $M_X = M_Y$ increases since the increasing thermal energy unbalances the anisotropic energy (which determines the [0 0 1] as the easy magnetic direction) and the magnetization vector direction displaces from the easy axis to the direction of the applied magnetic field. Then, depending on the thermal energy one can obtain $M_X = M_Y = M_Z$ at the [1 1 1] field direction. At 20 K all components are equal to $5.41\mu_B$ whereas at 62 K the common value is $3.54\mu_B$ (see Fig. 1(a)). It is important to mention that the temperature range for the spin reorientation can be tuned by selecting the intensity of the applied magnetic field. As an example, applying the field at the [1 1 0] direction for the intensity of 1 T we found T_{SR} (spin reorientation temperature) equal to 33.5 K whereas for 2 T the reorientation occurs at 23.5 K (not shown in this work).

The corresponding anisotropic entropy change can be calculated directly according to either $-\Delta S_{an}^{0-54.7^\circ} = S^{[1\,1\,1]} - S^{[0\,0\,1]}$ or using the Maxwell's relation (5) with $\phi = 45^\circ$ in the present case. From the experimental point of view, measurements in single crystals can provide the adequate quantities (namely $S^{[0\,0\,1]}$ and $S^{[1\,1\,1]}$) to determine this isothermal anisotropic-MCE. The $S^{[0\,0\,1]}$ and $S^{[1\,1\,1]}$ are determined, as example, by measurements of specific heat with applied field along the [0 0 1] and [1 1 1] directions, respectively. Otherwise, through magnetization data one can obtain the usual magnetocaloric effect ($-\Delta S$ *vs.* T) for these directions, *i.e.*, $-\Delta S^{[0\,0\,1]}$ and $-\Delta S^{[1\,1\,1]}$ for a field variation from $H_i = 0$ to H_f, so that $-\Delta S^{[0\,0\,1]} - (-\Delta S^{[1\,1\,1]}) = S^{[1\,1\,1]} - S^{[0\,0\,1]}$, since the zero-field entropy cancel mutually in the isothermic process. In Fig. 1(b) we reproduce the experimental data for the usual magnetocaloric effect in DyAl$_2$ by changing magnetic field along [0 0 1] and [1 1 1] directions [6]. The isothermal difference of these two curves gives the anisotropic entropy change (open diamonds symbols in Fig. 1(b)). Our calculations for $-\Delta S_{an}^{0-54.7^\circ}$ *vs.* T, either from relation (5) or by the difference of directional entropies (triangles and solid curve Fig. 1(b), respectively) is in good agreement with that obtained from experimental measurements. Observing the usual and anisotropic-MCE curves in Fig. 1(b), one can deduce the possibility to combine both quantities in order to improve the magnetocaloric effect. In fact, one can apply a field of 2 T along the [0 0 1] direction of the DyAl$_2$ single crystal and then rotate the crystal in such a way that the field ends oriented along the [1 1 0] direction. In this case, the anisotropic-MCE has higher values than those observed in conventional MCE, as reported in Ref. [10], for a region of temperatures around T_{SR} which permits to extend the range of temperatures for magnetic refrigeration using the MCE.

The TbNi$_2$ compound is a cubic ferromagnet with $T_C = 37$ K with the easy magnetic axis along the [1 1 1]-direction. For the calculations we use the same CEF and exchange parameters considered in Ref. [11] and the magnetic field intensity $H = 2$ T. Using the proposed model discussed above, we investigated the consequences of a magnetic field rotation from [1 0 0] to [1 1 0] direction in the x–y plane. The calculated thermal evolution of the magnetization components are illustrated in Fig. 2(a) where one can note kinks for the indicated field orientations (at $T = 32$ and 34 K for $\theta = 90^\circ$ and $\phi = 0^\circ$ and 45°) which are associated to second order spin reorientations. The vertical dotted lines at $T = 34$ K shows that only M_X component exist above $T = 34$ K, for $H = 2$ T applied along [1 0 0] direction. Similarly, the vertical dotted lines at $T = 32$ K shows that only M_X and M_Y components exist above $T = 32$ K, for $H = 2$ T applied along [1 1 0] direction. Note in Fig. 2(a) that $M_X = M_Y$ for $\phi = 45^\circ$ and $M_X = M_Y$ for $\phi = 0^\circ$ as expected due to the cubic symmetry.

In Fig. 2(b) we observe a type of signature in $-\Delta S_{an}$ between 32 and 34 K, a sharp change in the slope due to spin reorientation that takes place in the presence of the rotating field from [1 0 0] to [1 1 0] direction. Due to the fact that the transformation involves a change of second order nature, we used the Maxwell's relation (6) to obtain $-\Delta S_{an}$ in the total interval of temperatures (open squares) and one can observe the complete equivalence with direct calculations determined from $S^{[1\,1\,0]} - S^{[1\,0\,0]}$ (solid curve).

We considered the anisotropic-MCE model by exploring the cubic anisotropy in $DyAl_2$ and $TbNi_2$ rare earth intermetallic compounds with non-magnetic transition elements. However, it should be pointed out that the model applications can include other materials with more complex anisotropy and crystallographic symmetries.

On one hand, we know that uniaxial magnetocrystalline anisotropy is a desired characteristic in permanent magnetic materials but it is a source of several disadvantages for EMC due to energy loss effects. For this symmetry and considering the case of 3d–4f systems (with a magnetic partner for the rare earth ion), Kuz'min and Richter [12] have showed that the entropy change associated to spontaneous spin reorientation is too small to be considered in room-temperature magnetic refrigeration. Nevertheless, in 4f-based materials with strong anisotropy a magnetic refrigerator working on a rotating principle has been proposed [13]. As an example, one can considers the rotation of a $DyAlO_3$ single crystal in a magnetic field. The $DyAlO_3$ has very different effective magnetization along the [0 1 0] and [0 0 1] directions. Due to this fact, the magnetic entropy can change by switching the magnetic field between these directions [13]. In our study, we found advantages associated to field-induced spin reorientation such as competitive $-\Delta S_{an}$ intensity and the possibility to extend the operational temperature range to be used in EMC devices.

As well as the conventional MCE in ferromagnets show a peak in T_C (at ferromagnetic–paramagnetic transition temperature), the anisotropic-MCE in the studied compounds may be characterized by particular signatures at T_{SR}. Depending on the proximity of these temperatures the magnetocaloric curves can show either table-like or sharp-lambda type profiles as calculated in the cases described above and illustrated in Figs. 1(b) and 2(b), respectively.

4. Conclusions

We studied the effects of a continuous magnetic field rotation on the magnetic and magnetocaloric behavior with application in $DyAl_2$ and $TbNi_2$ simple cubic magnetic systems under anisotropy that comes from the CEF. For the $DyAl_2$ compound, where [0 0 1] is the easy magnetic direction, we have considered the [0 0 1]–[1 1 1] magnetic field rotation observing first order spin reorientation. For the $TbNi_2$ compound, where [1 1 1] is the easy magnetic direction, we have considered the [1 1 0]–[1 0 0] magnetic field rotation observing second order spin reorientation. The Maxwell-like formulation for the anisotropic-MCE has been introduced and applied to the above mentioned situations. The corresponding results for $-\Delta S_{an}$ were the same as the one calculated directly through directional entropies. The explicit evolution of the Cartesian components of magnetization revealed characteristics of the anisotropic-MCE curves (due to the order of transition and the separation between T_C and T_{SR}). However, magnetization discontinuities associated with first order spin reorientation must be adequately handled in the Maxwell-like relations.

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References

[1] V.K. Pecharsky, K.A. Gschneidner Jr., Phys. Rev. Lett. 78 (1997) 4494.
[2] V.K. Pecharsky, K.A. Gschneidner Jr., Appl. Phys. Lett. 70 (1997) 3299.
[3] T.W. Hill, W.E. Wallace, R.S. Craig, T.J. Inuone, Solid State Chem. 8 (1973) 364.
[4] Isaías G. de Oliveira, D.C. Garcia, P.J. von Ranke, J. Appl. Phys. 102 (2007) 073907.
[5] T. Morishita, K. Tsushima, IEEE Trans. Magn. 20 (1984) 1657.
[6] A.L. Lima, K.A. Gschneidner Jr., V.K. Pecharsky, J. Appl. Phys. 96 (2001) 2164.
[7] P.J. von Ranke, N.A. de Oliveira, C. Mello, D.C. Garcia, V.A. de Souza, A. Magnus, G. Carvalho, Phys. Rev. B 74 (2006) 054425.
[8] From a set of magnetic isofields one can obtain the usual MCE, $-\Delta S(T)$, using the Maxwellĩs differential equation $(\partial S/\partial H)_T = (\partial M/\partial T)_H$.
[9] P.J. von Ranke, N.A. de Oliveira, D.C. Garcia, V.S.R. de Souza, V.A. de Souza, A. Magnus, G. Carvalho, S. Gama, M.S. Reis, Phys. Rev. B 75 (2007) 184420.
[10] P.J. von Ranke, N.A. de Oliveira, E.J.R. Plaza, V.S.R. de Sousa, B.P. Alho, A. Magnus, G. Carvalho, S. Gama, M.S. Reis., J. Appl. Phys. 104 (2008) 093906.
[11] P.J. von Ranke, E.P. Nóbrega, I.G. de Oliveira, A.M. Gomes, R.S. Sarthour, Phys. Rev. B 63 (2001) 184406.
[12] Michael D. Kuz'min, Manuel Richter, Appl. Phys. Lett. 90 (2007) 132509.
[13] A.M. Tishin, Y.I. Spichkin, The Magnetocaloric Effect and its Applications, Taylor & Francis, Bristol, 2003.