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Magnetocaloric effect around a magnetic phase transition

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In this work we discuss the thermodynamics of the magnetocaloric effect around the first- and second-order magnetic phase transitions. We show that, around the second-order phase transition, the magnetocaloric potential ΔS can indeed be determined by using magnetization data through the Maxwell relation. However, around the first-order phase transition, the Maxwell relation is not valid so that the determination of ΔS by using magnetization data is somewhat more complex and should be done very carefully. These statements were verified in a simple model of interacting spins with two energy levels including an extra term to account for the first-order phase transition.

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I. INTRODUCTION

The magnetocaloric effect is characterized by the isothermal entropy change (ΔS) and by the adiabatic temperature change (ΔT_{ad}) upon variation of the applied magnetic field. The adiabatic temperature change can be measured directly or indirectly using heat-capacity and magnetization data.[1,2] The isothermal entropy change for a magnetic-field variation from B_0 to B_1 can be obtained by the integration of heat-capacity data through the relation $\Delta S(T,\Delta B)=S(T,B_1)-S(T,B_0)$, where $\Delta B=B_1-B_0$ and the entropy is given by $S=\int_0^T(C/T)dT$. Alternatively, using the Maxwell relation $(\partial S/\partial B)_T=(\partial M/\partial T)_B$, the isothermal entropy change can also be determined through the expression $\Delta S(T,\Delta B)=\int_{B_0}^{B_1}(\partial M/\partial T)dB$. It can be observed from this previous equation that the larger $(\partial M/\partial T)$ is, the larger ΔS becomes. Therefore, it is expected that the ΔS curve reaches its maximum value around the magnetic ordering temperature (T_C), where the partial derivative $(\partial M/\partial T)$ exhibits a peak. Due to experimental difficulties in measuring heat capacity, the Maxwell relation constitutes a good alternative to determine the isothermal entropy change. As a matter of fact, the relation $\Delta S(T,\Delta B)=\int_{B_0}^{B_1}(\partial M/\partial T)dB$ has been intensively used to obtain the isothermal entropy change upon magnetic-field variation; it is used independently if the magnetic phase transition is of second or first order. Undoubtedly, ΔS obtained by using this relation in compounds undergoing a second-order phase transition is very good. However, the validity[3–8] of the relation $\Delta S(T,\Delta B)=\int_{B_0}^{B_1}(\partial M/\partial T)dB$ to determine the isothermal entropy change in compounds undergoing a first-order phase transition is not clear yet and further studies are necessary to clarify this point.

The main goal of this work is to discuss the thermodynamics of the magnetocaloric effect, mainly around the first-order magnetic phase transition. In particular, we are interested in verifying whether or not the relation $\Delta S(T,\Delta B)=\int_{B_0}^{B_1}(\partial M/\partial T)dB$ can be used to determine the isothermal entropy change around the first-order phase transition. The complete understanding of this subject is very important not only to guide researchers to correctly determine the magnetocaloric potential ΔS through the magnetization data but also to establish the underlying physics behind the magnetocaloric effect around the first-order phase transition. In order to address this important issue, we discuss in Sec. II the thermodynamics of the magnetocaloric effect, considering the possibility of second- and first-order phase transitions. In order to illustrate the statements discussed in Sec. II, we use in Sec. III a simple model of interacting spins with two energy levels, including an extra term to account for the appearance of the first-order phase transition.

II. THERMODYNAMICS OF THE MAGNETOCALORIC EFFECT

In this section, we discuss the thermodynamics of the magnetocaloric effect in compounds undergoing both second- and first-order phase transitions. First, we discuss the determination of the isothermal entropy change from heat-capacity data. After that, we discuss the determination of the isothermal entropy change using magnetization data through the Maxwell relation. Generally speaking, the entropy of a solid is made up of a contribution from the magnetic ions, crystalline lattice, and conduction electrons. For the sake of simplicity, we consider that the total entropy of a solid can be written, as a sum of these three contributions, as

$$S(T,B)=S_{\mathrm{mag}}(T,B)+S_{\mathrm{lat}}(T)+S_{\mathrm{el}}(T), \tag{1}$$

where $S_{\mathrm{mag}}(T,B)$ is the contribution from the magnetic ions, $S_{\mathrm{lat}}(T)$ is the contribution from the crystalline lattice, and $S_{\mathrm{el}}(T)$ is the contribution from the conduction electrons. We suppose here that only the magnetic part of the entropy depends on the magnetic field. From the experimental point of view, the entropy curve can be constructed from heat-capacity measurements using the thermodynamical relation $S=\int(C/T)dT$, where C is the heat capacity. The isothermal entropy change upon magnetic-field variation can be obtained from the entropy vs temperature curves as $\Delta S(T,\Delta B)=S(T,B_1)-S(T,B_0)$. In terms of the specific-heat capacity, ΔS can be written as

$$\Delta S(T,\Delta B)=\int_0^T\frac{C(T,B_1)-C(T,B_0)}{T}dT. \tag{2}$$

In Fig. 1, it depicted an entropy vs temperature diagram showing the magnetocaloric potentials ΔS and ΔT_{ad}. It should be emphasized that ΔS, calculated in Eq. (2), is basi-

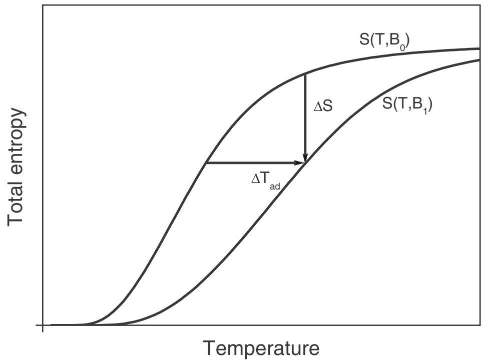

FIG. 1. Entropy vs temperature diagram illustrating the magnetocaloric potentials ΔS and ΔT_{ad}.

cally the magnetic entropy change since in our approximation, the crystalline lattice and electronic entropy are supposed to be magnetic-field independent. Equation (2) is valid for compounds undergoing both second- and first-order phase transitions. However, sometimes it is not so easy to obtain experimental data of heat capacity, mainly around a first-order phase transition. In order to discuss alternative ways to obtain the magnetocaloric potential ΔS, we consider the entropy of a given material as a function of temperature and magnetic field, i.e., $S(T,B)$. For an increment in temperature (δT) and in magnetic field (δB) the entropy change is

$$\delta S(T,B) = S(T+\delta T, B+\delta B) - S(T,B). \tag{3}$$

Adding the term $\pm S(T+\delta T,B)$ and using the mean value theorem from the fundamental calculus,[9] i.e., $f(T+\delta T) - f(T) = \delta T \cdot df(T_C)/dT$, where T_C lies between T and $T+\delta T$, we can write that

$$\delta S(T,B) = \left[\frac{\partial S(T_C,B)}{\partial T}\right]_B \delta T + \left[\frac{\partial S(T,B_C)}{\partial B}\right]_T \delta B, \tag{4}$$

where $\partial S(T_C,B)/\partial T$ and $\partial S(T,B_C)/\partial B$ means that the derivatives are calculated at the points T_C and B_C, respectively. The partial derivatives $\partial S(T_C,B)/\partial T$ and $\partial S(T,B_C)/\partial B$ can be written as[9]

$$\left[\frac{\partial S(T_C,B)}{\partial T}\right]_B = \left[\frac{\partial S(T,B)}{\partial T}\right]_B + \left[\frac{\delta S(T_C,B)}{\delta T}\right]_B \tag{5}$$

and

$$\left[\frac{\partial S(T,B_C)}{\partial B}\right]_T = \left[\frac{\partial S(T,B)}{\partial B}\right]_T + \left[\frac{\delta S(T,B_C)}{\delta B}\right]_T, \tag{6}$$

where $[\delta S(T_C,B)/\delta T]_B$ is the difference between the derivatives $(\partial S/\partial T)$ at the points T_C and T, and $[\delta S(T,B_C)/\delta B]_T$ is the difference between the derivatives $(\partial S/\partial B)$ at the points B_C and B. Putting Eqs. (5) and (6) into Eq. (4), we get that the change in the entropy in the infinitesimal limit can be written as

$$dS(T,B) = \left\{\left[\frac{\partial S(T,B)}{\partial T}\right]_B + \left[\frac{\delta S(T_C,B)}{\delta T}\right]_B\right\} dT + \left\{\left[\frac{\partial S(T,B)}{\partial B}\right]_T + \left[\frac{\delta S(T,B_C)}{\delta B}\right]_T\right\} dB. \tag{7}$$

In the cases of compounds undergoing a second-order phase transition, the entropy is a continuous function of temperature and magnetic field so that the terms $[\delta S(T_C,B)/\delta T]_B$ and $[\delta S(T,B_C)/\delta B]_T$ go to zero. Thus, for an isothermal process, the entropy change upon magnetic-field variation from B_0 to B_1 in compounds undergoing a second-order phase transition is calculated by integrating the Eq. (7) from B_0 to B_1, i.e.,

$$\Delta S(T,\Delta B) = \int_{B_0}^{B_1} \left[\frac{\partial S(T,B)}{\partial B}\right]_T dB, \tag{8}$$

where $\Delta S(T,\Delta B) = S(T,B_1) - S(T,B_0)$. In the cases of compounds undergoing a first-order phase transition, there is a discontinuity in the entropy function around the critical points T_C and B_C. In fact, there is a range of temperatures and magnetic fields, where the magnetic entropy and also the magnetization exhibit discontinuity (for details see Fig. 5). Therefore, in these cases, the total differential of the entropy should be written considering whether the temperature and the magnetic field are inside or outside the region, in which the first-order phase transition takes place. For temperatures and magnetic fields away from the first-order phase transition, the terms $[\delta S(T_C,B)/\delta T]_B$ and $[\delta S(T,B_C)/\delta B]_T$ also go to zero so that the entropy change in an isothermal process, calculated by integrating Eq. (7) from B_0 to B_1, is given by

$$\Delta S_{\mathrm{outside}}^{\mathrm{FO}}(T,\Delta B) = \left\{\int_{B_0}^{B_1} \left[\frac{\partial S(T,B)}{\partial B}\right]_T dB\right\}_{\mathrm{outside}}. \tag{9}$$

Here, we use the notation $S_{\mathrm{outside}}^{\mathrm{FO}}$ to characterize the entropy outside the temperature region of the first-order phase transition. At temperatures inside the region of the first-order phase transition, the term $[\delta S(T,B_C)/\delta B]_T$ in Eq. (7) is not zero so that the isothermal entropy change upon magnetic-field variation from B_0 to B_1 is obtained by integrating the second term in Eq. (7), i.e.,

$$\int_{B_0}^{B_1} dS_{\mathrm{inside}}^{\mathrm{FO}}(T,B) = \int_{B_0}^{B_1} \left\{\left[\frac{\partial S(T,B)}{\partial B}\right]_T + \left[\frac{\delta S(T,B_C)}{\delta B}\right]_T\right\} dB. \tag{10}$$

The first term involving the partial derivative $[\partial S(T,B)/\partial B]_T$ is only defined in the magnetic-field intervals $[B_0,B_C]$ and $[B_C+\delta B,B_1]$ where the entropy is a derivable function. On the other hand, the second term is only defined in the magnetic-field interval $[B_C,B_C+\delta B]$ where there is a jump in the entropy function. Using this consideration, the previous expression can be explicitly written as

$$\Delta S^{\mathrm{FO}}_{\mathrm{inside}}(T,\Delta B) = \int_{B_0}^{B_C}\left[\frac{\partial S(T,B)}{\partial B}\right]_T dB + \int_{B_C+\delta B}^{B_1}\left[\frac{\partial S(T,B)}{\partial B}\right]_T dB + \delta S(T,B_C), \tag{11}$$

where B_C is the critical magnetic field where the first-order phase transition takes place. Therefore, around the first-order phase transition, the isothermal entropy change should be determined by using Eq. (11) instead of Eq. (9). It is important to mention that from the operational point of view, there is no advantage in using Eqs. (8), (9), and (11) to evaluate the isothermal entropy change ΔS because it is easily obtained by using the relation (2). The great advantage of developing the relations (8)–(11) relies on the fact that they enable us to use magnetization data to obtain the isothermal entropy change. This aspect is addressed in the following lines.

In order to discuss the evaluation of ΔS using magnetization data, we consider the Gibbs free energy as a function of temperature and magnetic field, i.e., $G(T,B)$. The change in the free energy as the temperature goes from T to $T+\delta T$ and the magnetic field goes from B to $B+\delta B$ is given by

$$\delta G(T,B) = G(T+\delta T, B+\delta B) - G(T,B). \tag{12}$$

Following similar procedures used before, we can write in the infinitesimal limit that

$$dG(T,B) = \left\{\left[\frac{\partial G(T,B)}{\partial T}\right]_B + \left[\frac{\delta G(T_C,B)}{\delta T}\right]_B\right\}dT + \left\{\left[\frac{\partial G(T,B)}{\partial B}\right]_T + \left[\frac{\delta G(T,B_C)}{\delta B}\right]_T\right\}dB. \tag{13}$$

For compounds undergoing a second-order phase transition, $[\delta G(T_C,B)/\delta T]_B = [\delta G(T,B_C)/\delta B]_T = 0$. Using the thermodynamic relations $S=-[\partial G(T,B)/\partial T]_B$ and $M=-[\partial G(T,B)/\partial B]_T$, we can write the previous equation in the form $dG(T,B) = -S(T,B)dT - M(T,B)dB$. Since the free energy $G(T,B)$ is an exact differential, we can write the following Maxwell relation $[\partial S(T,B)/\partial B]_T = [\partial M(T,B)/\partial T]_B$. Using this Maxwell relation, the isothermal entropy change for compounds undergoing a second-order phase transition given in Eq. (8) can be written in terms of the magnetization as

$$\Delta S(T,\Delta B) = \int_{B_0}^{B_1}\left[\frac{\partial M(T,B)}{\partial T}\right]_B dB. \tag{14}$$

For practical purpose this equation can be approximately written in the form

$$\Delta S(T,\Delta B) = \int_{B_0}^{B_1}\frac{M(T+\delta T,B) - M(T,B)}{\delta T} dB, \tag{15}$$

where the curves $M\times B$ now can be used instead of the curves $M\times T$.

For compounds undergoing a first-order phase transition, we have to handle Eq. (13) very carefully. Let us separate the discussion in two distinct regions, namely: the region outside and inside the first-order phase transition. In the range of temperatures and magnetic fields outside the region of the first-order phase transition, we have $[\delta G(T_C,B)/\Delta T]_B = [\delta G(T,B_C)/\Delta B]_T = 0$. In this case, the free energy is also an exact differential so that the Maxwell relation $[\partial S(T,B)/\partial B]_T = [\partial M(T,B)/\partial T)]_B$ holds outside the region of the first-order phase transition. Therefore, it is valid to use the Maxwell relation $[\partial S(T,B)/\partial B]_T = [\partial M(T,B)/\partial T)]_B$ in Eq. (9) to calculate the isothermal entropy change far from the temperature region of the first-order phase transition as

$$\Delta S^{\mathrm{FO}}_{\mathrm{outside}}(T,\Delta B) = \left\{\int_{B_0}^{B_1}\left[\frac{\partial M(T,B)}{\partial T}\right]_B dB\right\}_{\mathrm{outside}}. \tag{16}$$

In the range of temperatures and magnetic fields inside the region of the first-order phase transition, the free energy in Eq. (13) turns out to be

$$dG^{\mathrm{FO}}_{\mathrm{inside}}(T,B) = \left\{\left[\frac{\delta G(T_C,B)}{\delta T}\right]_B\right\}_{\mathrm{inside}} dT + \left\{\left[\frac{\delta G(T,B_C)}{\delta B}\right]_T\right\}_{\mathrm{inside}} dB. \tag{17}$$

According to thermodynamics, the Gibbs free energy at the region of the first-order phase transition should fulfill the condition[10] $(G_P - G_F) = W_m$, where G_P and G_F are the free energy at the paramagnetic and ferromagnetic phases, respectively, and W_m is the magnetic work that will take the system from the paramagnetic state to the ferromagnetic one. From Eq. (17) the differential of the free energy at the paramagnetic and ferromagnetic phases around the first-order phase transition should be $dG_P^{\mathrm{FO}} = [\delta G_P(T_C,B)/\delta T]dT_C + [\delta G_P(T,B_C)/\delta B]dB_C$ and $dG_F^{\mathrm{FO}} = [\delta G_F(T_C,B)/\delta T]dT_C + [\delta G_F(T,B_C)/\delta B]dB_C$. Using these relations in the condition $dG_P = dG_F + dW_m$, we can write

$$(S_F^{\mathrm{FO}} - S_P^{\mathrm{FO}})dT_C = -(M_F^{\mathrm{FO}} - M_P^{\mathrm{FO}})dB_C + dW_m, \tag{18}$$

where $S_F^{\mathrm{FO}} = -\delta G_F(T_C,B)/\delta T$ and $M_F^{\mathrm{FO}} = -\delta G_F(T,B_C)/\delta B$. Similar relations hold for S_P^{FO} and M_P^{FO}. Defining $\delta S(T_C,B_C) = (S_F^{\mathrm{FO}} - S_P^{\mathrm{FO}})$ and $\delta M(T_C,B) = (M_F^{\mathrm{FO}} - M_P^{\mathrm{FO}})$, we can write

$$\delta S(T_C,B_C) = -\delta M(T_C,B)\frac{dB_C}{dT_C} + \frac{dW_m}{dT_C}. \tag{19}$$

The derivative of the magnetic work can be approximately written as $dW_m/dT_C \cong \frac{1}{2}\delta M(T_C,B)dB_C/dT_C$ (see Appendix), so that $\delta S(T_C,B_C)$ is approximately given by

$$\delta S(T_C,B_C) \cong -\frac{1}{2}\delta M(T_C,B)\frac{dB_C}{dT_C}. \tag{20}$$

Note that this equation is the corresponding Clausius-Clapeyron equation for magnetic systems undergoing first-order phase transition. The so-called magnetic Clausius-Clapeyron equation $[dB_c/dT_c = -\delta S/\delta M]$ commonly used in the literature[11,12] is not correct because it has been obtained by assuming the condition $dG_F = dG_P$, which is not valid for magnetic systems.[10] Putting $\delta S(T,B_C)$ into Eq. (11), the isothermal entropy change in the temperature range inside the region of the first-order phase transition should be determined using magnetization data as

$$\Delta S^{\mathrm{FO}}_{\mathrm{inside}}(T,\Delta B) \cong \int_{B_0}^{B_C} \left[\frac{\partial M(T,B)}{\partial T}\right]_B dB + \int_{B_C+\delta B}^{B_1} \left[\frac{\partial M(T,B)}{\partial T}\right]_B dB - \frac{1}{2}\delta M(T_C,B)\frac{dB_C}{dT_C}. \quad (21)$$

In the next section we develop a model of two energy levels in order to verify the results discussed in this section.

III. MODEL HAMILTONIAN AND THERMODYNAMIC RELATIONS

In order to illustrate the discussion about the thermodynamics of the magnetocaloric effect near the first- and second-order phase transitions, we consider a model of two energy levels including spin-spin interaction and the Zeeman term. The model Hamiltonian is

$$\mathcal{H} = -\sum_{il}[\lambda_0 \vec{J}_i \cdot \vec{J}_l + \lambda_1(\vec{J}_i \cdot \vec{J}_l)(\vec{J}_i \cdot \vec{J}_l)] - g\mu_B \sum_i \vec{J}_i \cdot \vec{B}. \quad (22)$$

The first term represents the usual spin-spin interaction where λ_0 is the exchange integral parameter. The second term accounts for the magnetoelastic coupling where λ_1 is a parameter of the model.[13,14] The third term is the Zeeman interaction between the magnetic moment and the magnetic field $\vec{B}$. In the mean-field approximation the model Hamiltonian turns out to be

$$\mathcal{H} = -g\mu_B \sum_i \left[\vec{B} + \frac{\lambda_0\langle\vec{J}\rangle + \lambda_1\langle\vec{J}\rangle^3}{g\mu_B}\right]\cdot \vec{J}_i. \quad (23)$$

Considering z as the easy magnetization direction and using the fact that $\vec{J}^z|J,m\rangle = m|J,m\rangle$, where $-J \le m \le J$, the energy eigenvalues of the above Hamiltonian per magnetic ion, for $J=1/2$, are $E_1 = [g\mu_B B + (\lambda_0\langle J^z\rangle + \lambda_1\langle J^z\rangle^3)]/2$ and $E_2 = -[g\mu_B B + (\lambda_0\langle J^z\rangle + \lambda_1\langle J^z\rangle^3)]/2$. Here $\langle J^z\rangle$ is the thermodynamical average given by $\langle j^z\rangle = \Sigma\langle J,m|J^z|J,m\rangle e^{-\beta E_1}/Z_{\mathrm{mag}}$, where $Z_{\mathrm{mag}} = e^{-\beta E_1} + e^{-\beta E_2} = 2\cosh(\beta E_1)$ is the partition function with $\beta = 1/k_B T$, k_B being the Boltzmann constant. The free energy is $G(T,B) = -k_B T \ln[2\cosh(\beta E_1)]$. The magnetization is $M = -[\partial G/\partial B]_T = \frac{1}{2}g\mu_B \tanh(\beta E_1)$. The magnetic entropy of this two energy-level model, calculated by $S_{\mathrm{mag}} = -[\partial G/\partial T]_B$, is given by

$$S_{\mathrm{mag}}(T,B) = k_B \ln[2\cosh(\beta E_1)] - \frac{E_1}{T}[\tanh(\beta E_1)]. \quad (24)$$

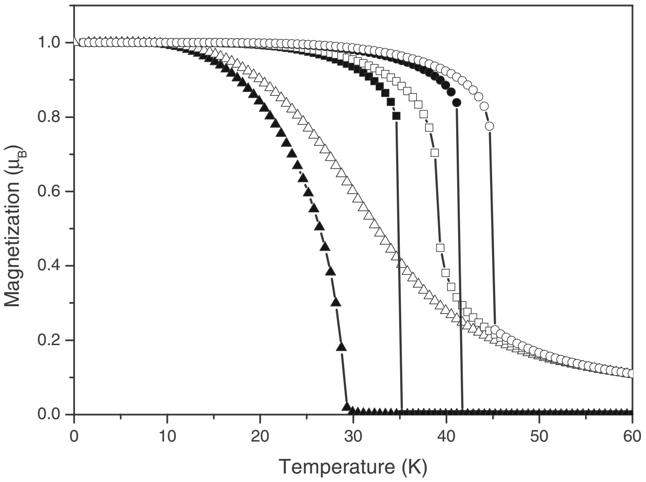

FIG. 2. Temperature dependence of the magnetization for $B=0$ (solid symbols) and $B=5$ T (open symbols). Triangles, squares, and circles represent the calculations for $\lambda_1 = 0$, 40, and 60 meV, respectively. $\lambda_0 = 10$ meV for all curves.

The total entropy is $S(T,B) = S_{\mathrm{mag}}(T,B) + S_{\mathrm{lat}}(T) + S_{\mathrm{el}}(T)$, where $S_{\mathrm{lat}}(T)$ is the lattice entropy calculated in the Debye approximation. Here $S_{\mathrm{el}}(T) = \gamma T$ is the electronic entropy where γ is the Sommerfeld coefficient. For the approximation used here, the entropy change upon magnetic-field variation is only the magnetic entropy change once $S_{\mathrm{lat}}(T)$ and $S_{\mathrm{el}}(T)$ do not depend on the applied magnetic field.

IV. NUMERICAL RESULTS

In this section we show the calculations of the magnetocaloric potential ΔS in the two energy-level models described in the previous section. When the magnetoelastic interaction is absent, the system undergoes a second-order magnetic phase transition. When the magnetoelastic interaction is turned on, the magnetic phase transition changes from second to first order above a critical value of the magnetoelastic coupling parameter λ_1. The larger the parameter λ_1, the stronger the first-order phase transition and the higher the magnetic ordering temperature. In Fig. 2, we plot the magnetization curves for $B=0$ T (solid symbols) and $B=5$ T (open symbols). The curves for the set of parameters ($\lambda_0 = 10$ meV and $\lambda_1 = 0$ meV), where the phase transition is of second order around 29 K, are represented by triangles. The curves for the set of parameters ($\lambda_0 = 10$ meV and $\lambda_1 = 40$ meV) and ($\lambda_0 = 10$ meV and $\lambda_1 = 60$ meV), where the phase transition is of first order around 35.2 and 41.5 K, are represented by squares and circles, respectively. For the same set of model parameters, the corresponding magnetic entropies in the absence of magnetic field and in a magnetic field of 5 T are represented in Fig. 3 by solid and open symbols, respectively.

In this work, we are only interested in the calculation of the isothermal entropy change. Since in our approximation, the electronic and the lattice entropy do not depend on the magnetic field, the isothermal entropy change upon magnetic-field variation comes only from the magnetic part of the entropy. We calculate the isothermal entropy change using the entropy curves shown in Fig. 3 and from Eq. (14)

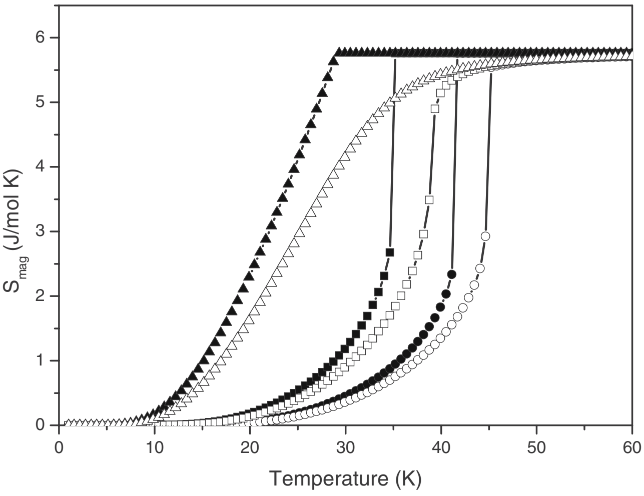

FIG. 3. Magnetic entropy for $B=0$ (solid symbols) and $B=5$ T (open symbols). Triangles, squares, and circles represent the calculations for $\lambda_1=0$, 40, and 60 meV, respectively. $\lambda_0=10$ meV for all curves.

using magnetization data for five different sets of model parameters, namely: (1) ($\lambda_0=10$ meV and $\lambda_1=0$ meV), (2) ($\lambda_0=10$ meV and $\lambda_1=20$ meV), (3) ($\lambda_0=10$ meV and $\lambda_1=30$ meV), (4) ($\lambda_0=10$ meV and $\lambda_1=40$ meV), and (5) ($\lambda_0=10$ meV and $\lambda_1=60$ meV). The obtained curves of the isothermal entropy changes are plotted in Fig. 4. In this figure, the solid lines represent the calculations from the entropy curves and the dotted lines plus symbols represent the calculation from Eq. (14) using magnetization data. In the case of the set of parameters ($\lambda_0=10$ meV and $\lambda_1=0$ meV) where system undergoes a second-order phase transition, the isothermal entropy change calculated from the entropy curves and the corresponding one obtained via the Maxwell relation are coincident, as can be seen in curve 1. In the case of the set of parameters ($\lambda_0=10$ meV and $\lambda_1=20$ meV) where the system is on the verge of the first-order phase transition, the isothermal entropy changes calculated from both methods are still similar to each other, as it is shown by curve 2.

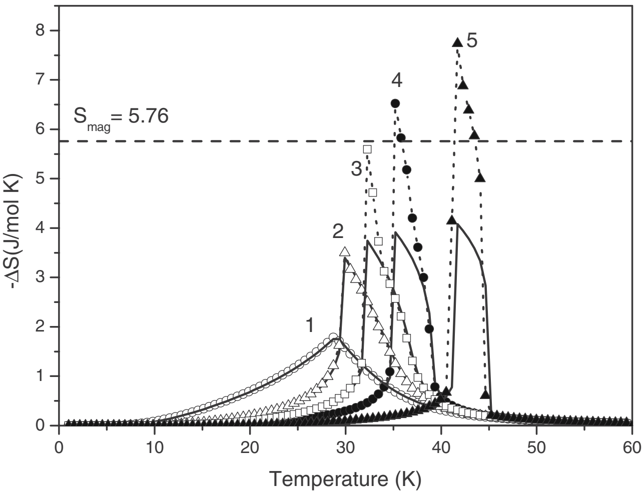

FIG. 4. Isothermal entropy change for a magnetic-field variation from 0 to 5 T. The curves 1–5 represent the calculation for $\lambda_1=0$, 20, 30, 40, and 60 meV, respectively. For all curves $\lambda_0=10$ meV. Solid lines represent the calculation from the entropy curves while dotted lines plus symbols represent the calculation through Eq. (14) using magnetization data. The dashed horizontal line represents the saturation value of the magnetic entropy.

In the cases of the sets of model parameters ($\lambda_0=10$ meV and $\lambda_1=30$ meV), ($\lambda_0=10$ meV and $\lambda_1=40$ meV), and ($\lambda_0=10$ meV and $\lambda_1=60$ meV) where the system undergoes a first-order phase transition, the isothermal entropy changes calculated from the entropy curves and those obtained from Eq. (14) are coincident only outside the region of the first-order phase transition as can be seen in the curves 3–5. However, at the region of the first-order phase transition, the calculated values of ΔS obtained from Eq. (14) using magnetization data are larger than the corresponding ones obtained from the entropy curves. The calculations show that the stronger the first-order phase transition, the larger the difference between ΔS calculated from the entropy curves and from Eq. (14) using magnetization data. Another interesting aspect shown in Fig. 4 is that the ΔS around the first-order phase transition represented in the curves 4 and 5, calculated from Eq. (14), are larger than the well-known saturation value of the magnetic entropy, i.e., $S_{mag}^{max}=R\ln(2J+1)$, which in our case of $J=1/2$ is $S_{mag}^{max}=5.76$ J/(mol K). As in our model, the entropy change is only the magnetic entropy change; its maximum value must not surpass the upper limit of the magnetic entropy given by $S_{mag}^{max}=5.76$ J/(mol K). Therefore, the curves 4 and 5 shown in Fig. 4 confirm that the calculations of ΔS through Eq. (14) using magnetization data indeed does not apply in the region of first-order phase transition because the obtained values overestimate the upper physical limit of the magnetic entropy variation.

In order to discuss somewhat more this discrepancy between the calculation of ΔS using the two referenced methods, we plot in Fig. 5, for the set of model parameters ($\lambda_0=10$ meV and $\lambda_1=40$ meV) where the system undergoes a first-order phase transition around 35 K, the magnetization as a function of the applied magnetic field in the range of temperatures from 31.0 to 40.61 K. In the temperature interval below the magnetic ordering temperature from 31.0 to 34.43 K, represented in Fig. 5 by the solid lines, the magnetization curves are monotonic functions of the applied magnetic field. As a result, the isothermal entropy changes calculated from Eq. (14), which is basically the difference between the area under the magnetization curves for two consecutive values of temperature per temperature interval, are exactly the same as the ones obtained from the entropy curves, as can be observed in the corresponding ΔS curve (curve 4) shown in Fig. 4. The same discussion also applies to temperature range above the magnetic ordering temperature from 39.23 to 40.61 K, represented by the dashed lines in Fig. 5. However, in the temperature range from 35.12 to 38.55 K, where the first-order phase transition takes place, the magnetization curves represented by the open circles in Fig. 5 exhibit jumps at a given applied magnetic field. In this range of temperatures, the isothermal entropy change, calculated by the difference between the areas under the magnetization curves for two consecutive values of temperature, is larger than the one

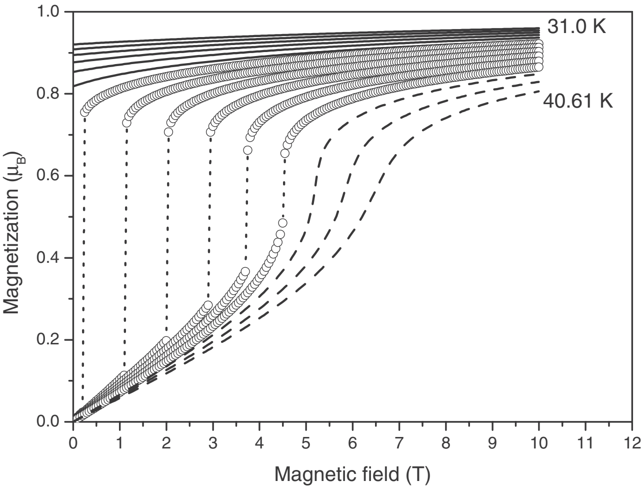

FIG. 5. Magnetization as a function of the magnetic field for $\lambda_0=10$ meV and $\lambda_1=40$ meV. Solid lines represent the isotherms below T_C from 31.0 to 34.43 K. Open circles represent the isotherms inside the region of the first-order phase transition from 35.12 to 38.55 K. Dashed lines represent the isotherms above T_C from 39.23 to 40.61 K.

obtained from the entropy vs temperature curves and can surpass the upper limit of the magnetic entropy. Such a result is an artifact of the calculations and does not have any physical means. Therefore, the calculations of ΔS through Eq. (14) in the two energy-level models show that this equation does not apply to the first-order phase transition, as we have shown in Sec. II by using thermodynamical principles. In fact, around the first-order phase transition, the isothermal entropy change should be calculated by Eq. (21).

Now, we use Eq. (21) to calculate the isothermal entropy change in the temperature range from 35.12 to 38.55 K inside the region of first-order phase transition. In order to illustrate the process of calculations, we plot in Fig. 6 only two magnetization isotherms for the consecutive temperatures of 35.81 and 36.49 K. The first and the second terms in Eq. (21) respectively represent the difference in the area under the magnetization curves in the magnetic-field regions 1 and 3, as shown in Fig. 6. In the magnetic-field region 2, where the first-order phase transition takes place, the entropy change must be calculated by the Clausius-Clapeyron like equation, represented by the third term in Eq. (21). In order to determine the contribution of the third term in Eq. (21), we first determine from the magnetization isotherms the critical magnetic field as a function of temperature. Then we plot the curve B_C vs T and determine the derivative dB_C/dT_C. After that, using the magnetization change at the critical field B_C, also extracted from the magnetization isotherms, we determine the entropy change involved in the first-order phase transition at the magnetic critical field B_C. In Fig. 7, we plot B_C vs T together with the derivative dB_C/dT_C for the set of model parameters ($\lambda_0=10$ meV and $\lambda_1=40$ meV).

In Fig. 8, we plot the isothermal entropy change for the set of model parameters ($\lambda_0=10$ meV and $\lambda_1=40$ meV) and ($\lambda_0=10$ meV and $\lambda_1=60$ meV) calculated via Eqs. (14) and (21) (dotted lines and open symbols, respectively) using

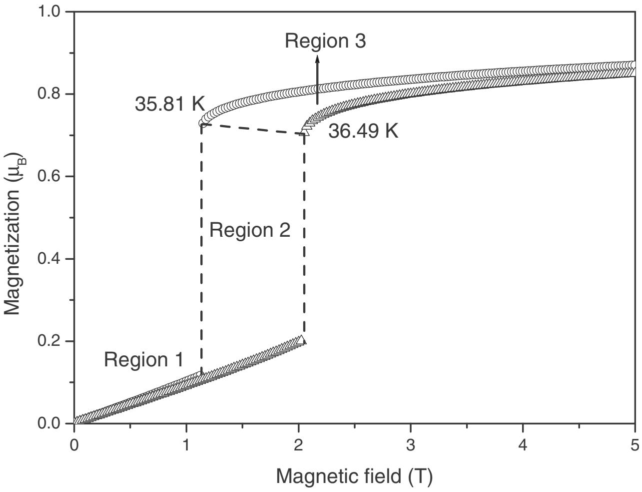

FIG. 6. Magnetization as a function of the magnetic field for $\lambda_0=10$ meV and $\lambda_1=40$ meV for the temperatures 35.81 and 36.49 K. The dashed lines delimit three regions, namely: region 1 and 3 outside the first-order phase transition, and region 2 inside the first-order phase transition.

magnetization data. The calculations of ΔS from Eq. (2) using the entropy curves are represented by solid lines. Notice that outside the region of the first-order phase transition, ΔS, which was calculated from different methods, agrees quite well. However, in the temperature range inside the first-order phase transition only ΔS calculated from the entropy curves (solid lines) and from Eq. (21) (open symbols) are coincident. The values of ΔS calculated from Eq. (14) (dotted lines) are overestimated and do not correspond to the physical reality. Notice that if we include the area of the trapezoidal figure (region 2 in Fig. 6) in the calculations, as it is done in the case of Eq. (14), the obtained values of ΔS around the first-order phase transition are overestimated, as can be seen from the dotted lines in Fig. 8. On the other hand, if we do not include this area in the calculation of ΔS, as it is done in the first two terms of Eq. (21), the obtained values of ΔS are

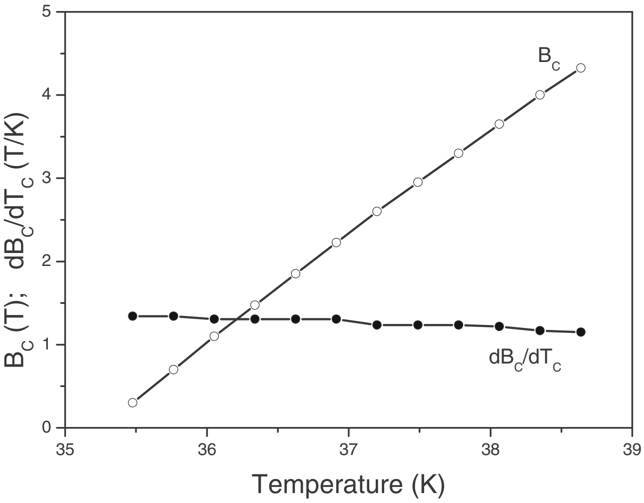

FIG. 7. Critical magnetic field B_C as a function of temperature for $\lambda_0=10$ meV and $\lambda_1=40$ meV (open circles). Solid circles represent dB_C/dT_C.

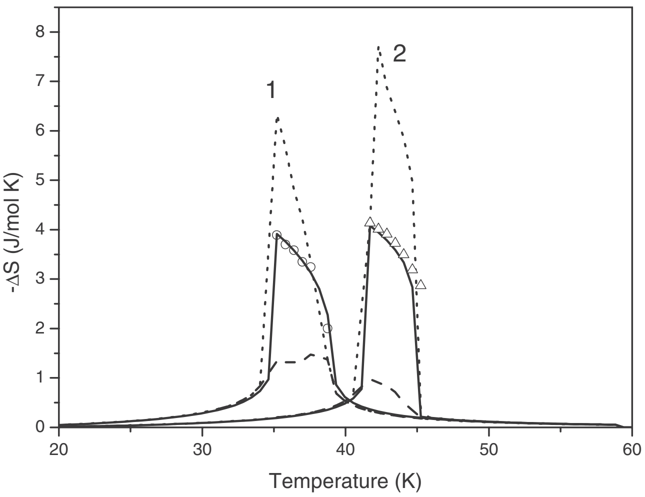

FIG. 8. Isothermal entropy change for $\lambda_1=40$ meV (set of curve 1) and $\lambda_1=60$ meV (set of curve 2) upon a magnetic-field variation from 0 to 5 T. For all curves, $\lambda_0=10$ meV. Open symbols represent the isothermal entropy change around the first-order transition, obtained through Eq. (21) using magnetization data, while solid lines represent ΔS obtained from the entropy curves. Dotted lines represent ΔS calculated through Eq. (14) using magnetization data. Dashed lines represent only the contributions from the two first terms in Eq. (21).

underestimated, as can be seen by the dashed lines in Fig. 8. Therefore, inside the region of the first-order phase transition, the correct calculation of ΔS, using magnetization data, must be done through Eq. (21).

In conclusion, in this work we discuss the thermodynamics of the magnetocaloric effect around the magnetic phase transition. Our calculations show that the isothermal entropy change in compounds undergoing a second-order phase transition can be determined by using either heat capacity or magnetization data through Eq. (14). However, we clearly show that from the basic concepts of thermodynamics, which do not depend on any physical model, the Eq. (14) is not valid for calculating the isothermal entropy change around a first-order phase transition. Such a statement has also been verified by using a simple two energy-level model. It should be emphasized that this conclusion is not restricted to the two energy-level model and is also true for any model Hamiltonian describing first-order phase transition. In the temperature region around the first-order phase transition, the determination of ΔS, using magnetization data through the Maxwell relation $\partial S/\partial B=\partial M/\partial T$, should be done very carefully and the result should be confirmed by specific-heat measurements.

ACKNOWLEDGMENTS

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APPENDIX

A magnetic body with a given magnetization has an intrinsic magnetic energy associated with it. To magnetize this body it is necessary to provide energy to align the magnetic moments in a preferable direction. In order to calculate the magnetic energy associated with a magnetic body, let us consider that it is made up of a great number of small pieces with a given magnetic moment.[15] Let us suppose that we can build the magnetic body by bringing each one of the small pieces from the infinity into the body. To bring the first magnetic piece from the infinity into the magnetic body, it is not necessary to do magnetic work. In order to bring the remaining magnetic pieces into the body, it is necessary to do work. The work needed to bring the second magnetic piece into the body, in presence of the first one, is equal to magnetic energy interaction between the two magnetic pieces. The magnetic energy interaction between these two pieces is then given by

$$U_m=-m_1B_2, \tag{25}$$

where m_1 is the magnetic moment of the first piece and B_2 is the magnetic field of the second magnetic piece. In the same way, when the third piece is brought into the body in presence of the two pieces already there, the magnetic energy interaction will be

$$U_m=-(m_1B_2+m_1B_3+m_2B_3). \tag{26}$$

This procedure is repeated to bring all the pieces into the magnetic body. In this case, the magnetic energy is given by

$$\begin{aligned}U_m=-(&m_1B_2+m_1B_3+m_2B_3+m_1B_4+m_2B_2\\&+m_3B_4\ldots m_1B_j),\end{aligned} \tag{27}$$

or in a more compact form as

$$U_m=-\frac{1}{2}\left(\sum_i m_i\right)\left(\sum_j B_j\right). \tag{28}$$

The factor 1/2 appears to avoid the double counting in the summation. Its physical meaning is related to the magnetic interactions into the magnetic body. Using the definition of magnetization $M=(1/V)\Sigma_i m_i$ and taking $B=\Sigma_j B_j$ as the total magnetic field inside the magnetic body, the magnetic energy per volume can be written as

$$U_m=-\frac{1}{2}M\cdot B, \tag{29}$$

When the system is in the ferromagnetic phase, the magnetic energy is then

$$U_m^F=-\frac{1}{2}M_F\cdot B_F, \tag{30}$$

where M_F and B_F are respectively the magnetization and the magnetic field in the ferromagnetic phase. Similarly, when the system is in the paramagnetic phase, the energy is given by

$$U_m^P=-\frac{1}{2}M_P\cdot B_C, \tag{31}$$

where M_P and B_C are respectively the magnetization and the magnetic field in the paramagnetic phase. The magnetic work necessary to bring the system from the paramagnetic phase to the ferromagnetic one is equal to the difference between the magnetic energy of these two states, i.e.,

$$W_m = -\,(U_m^F - U_m^P) = \frac{1}{2}(M_F \cdot B_F - M_P \,.\, B_C). \tag{32}$$

Supposing $B_F = B_C + \delta B$, we can write the magnetic work as

$$W_m = \frac{1}{2}B_C \delta M + \frac{1}{2}M_F \cdot \delta B, \tag{33}$$

where $\delta M = (M_F - M_P)$. In the limit where $\delta B \rightarrow 0$ and neglecting the changes in δM around T_C, we get that the derivative dW_m / dT_C can be approximately written as

$$\frac{dW_m}{dT_C} \cong \frac{1}{2}\delta M(T_C,B)\frac{dB_C}{dT_C}. \tag{34}$$

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[1] V. K. Pecharsky and K. A. Gschneidner, Jr., J. Magn. Magn. Mater. **200**, 44 (1999).

[2] V. K. Pecharsky and K. A. Gschneidner, Jr., J. Appl. Phys. **86**, 565 (1999).

[3] A. M. Tishin, K. A. Gschneidner, and V. K. Pecharsky, Jr., Phys. Rev. B **59**, 503 (1999).

[4] A. Giguère, M. Foldeaki, B. Ravi Gopal, R. Chahine, T. K. Bose, A. Frydman, and J. A. Barclay, Phys. Rev. Lett. **83**, 2262 (1999).

[5] K. A. Gschneidner, Jr., V. K. Pecharsky, E. Brück, H. G. M. Duijn, and E. M. Levin, Phys. Rev. Lett. **85**, 4190 (2000).

[6] J. R. Sun, F. X. Hu, and B. G. Shen, Phys. Rev. Lett. **85**, 4191 (2000).

[7] M. Földeàki, R. Chahine, T. K. Bose, and J. A. Barclay, Phys. Rev. Lett. **85**, 4192 (2000).

[8] G. J. Liu, J. R. Sun, J. Shen, B. Gao, H. W. Zhang, F. X. Hu, and B. G. Shen, Appl. Phys. Lett. **90**, 032507 (2007).

[9] M. L. Boas, *Mathematical Methods in the Physical Sciences*, 2nd ed. (Wiley, New York, 1966), p. 152.

[10] F. Reif, *Fundamentals of Statiscal and Thermal Physics* (McGraw-Hill, London, 1984), p. 296.

[11] K. A. Gschneidner, Jr., V. K. Pecharsky, and A. O. Tsokol, Rep. Prog. Phys. **68**, 1479 (2005).

[12] A. M. Tishin and Y. I. Spichkin, *The Magnetocaloric Effect and its Applications* (Institute of Physics, Bristol, 2003), p. 31.

[13] C. Kittel, Phys. Rev. **120**, 335 (1960).

[14] N. A. de Oliveira, Appl. Phys. Lett. **90**, 052501 (2007).

[15] D. Gignoux and J. C. Peuzin, *Magnetostatique*, Magnétistme-Fondements Vol. I (Grenoble Sciences EDP Sciences, Paris, 2000), pp. 69–71.