The effect of magnetic irreversibility on estimating the magnetocaloric effect from magnetization measurements

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We found that the anomalous magnetic entropy change peak obtained from magnetization measurements in some first-order magnetic phase transition materials may result from the usual data analysis procedure, which does not take into account magnetic irreversibility or mixed-phase regime. The deviations produced are comparable to anomalous effects discussed in the literature and may even exceed the theoretical limit. Our results show that this anomalous magnetic entropy change peak should not necessarily be interpreted as a consequence of the particular physics of the studied system. This also explains its absence in specific heat measurements. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3075851]

The study of the magnetocaloric effect (MCE) received a major impetus by the discovery of the giant MCE of the $Gd_5Si_2Ge_2$ alloy by the group of Pecharsky and Gschneidner in 1997.[1] This has driven the now very active field of research into the study of other giant MCE materials, including $MnAs_{1-x}Sb_x$,[2] $LaFe_{11.4}Si_{1.6}$,[3] $MnFeP_{0.45}As_{0.55}$,[4] and $Ni_{55}Mn_{20}Ga_{25}$ shape-memory alloy.[5] Further, the discovery of the colossal MCE has been reported either pressure-induced in MnAs,[6] or at ambient pressure in $Mn_{1-x}Fe_xAs$ (Ref. 7) and $Mn_{1-x}Cu_xAs$.[8] One common property among these materials is that they all undergo a first-order magnetic or magnetostructural phase transition.

Some points are currently under discussion regarding the reported entropy change of these first-order phase transition systems. These include the disagreement between calorimetric and magnetization results, as discussed by Giguere *et al.*[9] for the $Gd_5Si_2Ge_2$ alloy, and further discussed by Pecharsky and Gschneidner,[10] with similar situations in other systems.[11,12] In the case of M versus H measurements with visible hysteresis,[5,9] the use of the Maxwell relation also yields distinct ΔS_M values for field-increasing and field-decreasing magnetization curves.

The isothermal magnetic entropy change of these materials is commonly estimated indirectly from magnetic measurements and the use of the Maxwell relation,

$$\left(\frac{\partial S}{\partial H}\right)_T = \left(\frac{\partial M}{\partial T}\right)_H, \tag{1}$$

to yield the isothermal magnetic entropy change ΔS_M induced by a magnetic field change. This is usually done with a numerical approximation of the integral

$$|\Delta S_M| = \int \left(\frac{\partial M}{\partial T}\right) dH \simeq \sum \frac{(M_n - M_{n+1})_H}{T_{n+1} - T_n} \Delta H_n, \tag{2}$$

where n represents the sequence of experimental measured points or a convenient average.

Recently, the use of Eq. (2) on the magnetization data of MnAs was discussed by Liu *et al.*,[13] who suggested a graphical correction to the estimation of ΔS_M from magnetization measurements. The authors argued that the coexistence of paramagnetic (PM) and ferromagnetic (FM) phases in a mixed-phase first-order phase transition makes the use of the Maxwell relation overestimate ΔS_M and consequently considered the high values of entropy change as a spurious result.

The use of Eqs. (1) and (2) is only valid if the system is in thermodynamic equilibrium. If there occurs a first-order magnetic phase transition, magnetization values that do not correspond to the equilibrium value can be measured, and the measurement then depends on the kinetics of the phase transition, and consequently also on the experimental procedure. So, there is an approximation when using Eq. (1) to estimate ΔS_M from magnetization data from a first-order phase transition system, since the possible metastable nature of the measured state is not taken into consideration.

In this work, we study the effects of this common approximation, taking into account irreversibility and the existence of metastable states. Our approach is to use simple models that describe the general properties of a first-order magnetic phase transition: the Landau theory of phase transitions and the molecular mean-field model. The Landau theory has been shown to adequately describe several types of systems, including those related to magnetocaloric studies.[14–16]

In the framework of the Landau theory, a first-order magnetic phase transition can be described within the energy expansion,

$$G(T,M) = G_0 + \tfrac{1}{2}AM^2 + \tfrac{1}{4}BM^4 + \tfrac{1}{6}CM^6 - MH, \tag{3}$$

by considering $A = A'(T - T_C)$, $B < 0$, and $C > 0$.[17] The negative B value can be described as a consequence of magnetoelastic coupling and has been shown to affect the value of ΔS_M.[18] Within the Landau framework, magnetic entropy can be determined from

$$S_M(T,H) = -\left(\frac{\partial G}{\partial T}\right)_H. \tag{4}$$

In the simplest case, B and C can be taken as temperature-independent and the magnetic entropy is simply $-1/2(A'M^2)$, from Eq. (4). For a more general case, see Ref. 18. By considering the two free energy minima of G, the limits of the metastability region are defined, which, in a

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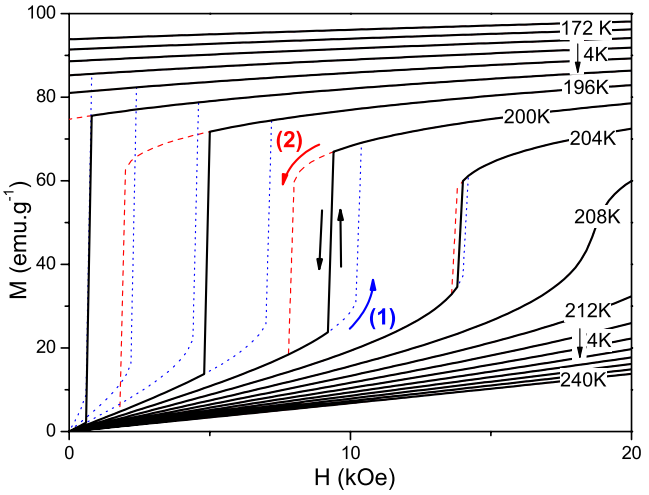

FIG. 1. (Color online) M vs H isotherms from Landau theory, for a first-order transition with equilibrium (solid lines) and nonequilibrium (dashed and dotted lines).

simplified approach, can be considered as the kinetic limit in terms of observing these metastable states. The equilibrium solution arises from the absolute minimum of free energy.

Figure 1 shows M versus H data resulting from the use of Landau coefficients that describe a magnetovolume induced first-order phase transition material with $T_C \sim 195$ K: $A=25(T-180)$ (g Oe emu^{-1}), $B=-0.18$ (g Oe emu^{-1})^3, and $C=2.33\times10^{-5}$ (g Oe emu^{-1})^5. The metastable limits are presented, in analogy to increasing and decreasing field measurements.

We use the three sets of curves and with the usual procedure of using Eq. (2), we estimate ΔS_M for equilibrium and the two metastable limits, where $\Delta S_M = S_M(T,H) - S_M(T,0)$. We compare these results with the use of the free energy derivative [Eq. (4)] as shown in Fig. 2.

The use of the Maxwell relation on this nonequilibrium data produces visible deviations, and in the case of metastable solution (2), the obtained peak shape is quite similar to that reported by Pecharsky and Gschneidner for $Gd_5Si_2Ge_2$.[10] In this case $\Delta S_M(T)$ values from caloric measurements follow the half-bell shape of the equilibrium solution, but from magnetization measurements, an obvious sharp peak in $\Delta S_M(T)$ appears. Similar deviations have been interpreted as a result of numerical artifacts,[2] but are not present in a first-order system with no visible hysteresis.[3]

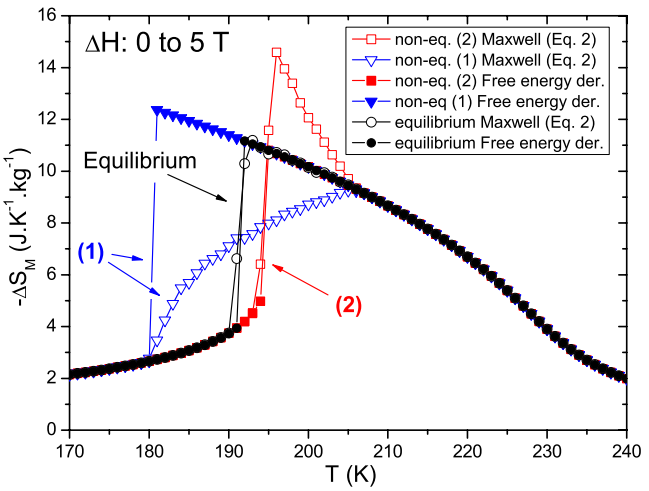

FIG. 2. (Color online) ΔS_M vs T for equilibrium and nonequilibrium solutions from Maxwell relation (open symbols) or from Eq. (4) (full symbols) for Landau theory M vs H data from 0 to 5 T.

It is of interest to verify if this overestimation of ΔS_M holds up in higher fields and eventually exceeds the theoretical limit of magnetic entropy change, as well as to consider a stronger first-order transition, with a consequently larger T and H regions with magnetic irreversibility.

Since values of M near saturation need to be considered, we use the molecular mean-field model. Here the entropy change from an applied magnetic field variation of $\Delta H = H_2 - H_1$ can conveniently be expressed as a function of magnetization change,

$$-\Delta S_M(T)_{\Delta H} = \int_{M|_{H_1}}^{M|_{H_2}} \left[f^{-1}(M) - \left(\frac{\partial \lambda}{\partial T}\right)_M M \right] dM, \qquad (5)$$

where λ is the mean-field exchange parameter, f is a mean-field state function (for instance the Brillouin function), following $M=f[(H+H_{\text{exch}})/T]$. The use of Eq. (5) was recently shown to be comparable to the results from Eq. (2), for systems with first- and second-order magnetic transition.[19] For our analysis, the molecular exchange field is taken as $H_{\text{exch}} = \lambda_1 M + \lambda_3 M^3$, where λ_3 describes magnetovolume effects, following the Bean and Rodbell formulation.[20] The value of λ_1 was chosen to give a $\Theta_p \sim 300$ K. We have not introduced any dependence of λ on T. The Brillouin function was used, with a spin of $J=2$ and $g=2$, and the saturation magnetization value was set to 100 emu g^{-1}. These values aim to generally represent a first-order phase transition, not a particular magnetic system.

M versus H curves for a first-order magnetic transition, with a region of irreversibility between 300 and 316 K, and critical field of 2.5 T, resulting from a λ_3 parameter equal to 1.5 (Oe g emu^{-1})^3, were calculated. The Maxwell construction[21] was used to determine the equilibrium solution (matching of the energy of the two phases).

Like the results from the Landau theory, we can compare ΔS_M from a model-specific relation [Eq. (5)] to results from the Maxwell relation for equilibrium and nonequilibrium solutions. For the parameter values shown above, the overestimation of ΔS_M from using the Maxwell relation in nonequilibrium can be as high as $\frac{1}{3}$ of the value obtained under equilibrium, for an applied field change of 5 T.

For large values of H, where M is near saturation in the PM region, the upper limit to magnetic entropy change, $\Delta S_M(\max) = Nk_B \ln(2J+1)$, is reached, which for the chosen model parameters is ~ 60 J K^{-1} kg^{-1}. However, this is in excess by around 10% by the use of the Maxwell relation to nonequilibrium values. If a stronger magnetovolume coupling is considered [$\lambda_3=8$ (Oe g emu^{-1})^3], the limit can be in excess by ~ 30 J K^{-1} kg^{-1}, clearly breaking the thermodynamic limit of the model and falsely producing a colossal MCE.

The mean-field model also allows the study of mixed-state transitions by considering a proportion of phases (high and low magnetization) within the metastability region. Magnetization curves are shown in the inset of Fig. 3, for $\lambda_3=2$ (Oe g emu^{-1})^3, corresponding to a critical field ~ 10 T. The mixed-phase temperature region is from 328 to

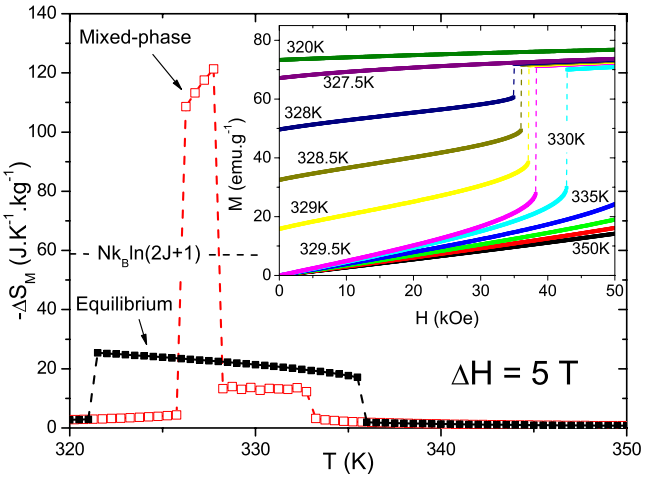

FIG. 3. (Color online) Inset: M vs H isotherms of a mixed-phase system from the mean-field model. Main figure: corresponding $\Delta S_M(T)$ for $\Delta H = 5$ T from Maxwell relation (open symbols) and of the equilibrium solution (solid symbols).

329 K, where the proportion of FM phase is set to 25% at 329 K, 50% at 328.5 K, and 75% at 328 K.

The deviation resulting from using the mixed-state M versus H curves and Eq. (2) to estimate ΔS_M is now larger compared to the previous results, as shown in Fig. 3, since now the system is also inhomogeneous, further invalidating the use of the Maxwell relation. The thermodynamic limit to entropy change is again falsely broken. Note how the temperatures that exceed the limit of entropy change are the ones that include mixed-phase data to calculate ΔS_M from Eq. (2).

This result shows how the estimated value of ΔS_M can be greatly increased solely as a consequence of using the Maxwell relation on magnetization data from a mixed-state transition, which is the case of materials that show a colossal MCE.[13] It is worth noting that, at this time, there are no calorimetric measurements that confirm the existence of the colossal MCE and its discovery came from magnetization data and the use of the Maxwell relation.

In conclusion, we studied the effect of estimating ΔS_M from nonequilibrium magnetization data. The usual data analysis procedure of estimating magnetic entropy change does not take into account magnetic irreversibility nor a mixed-phase regime and the results can present an anomalous peak. The presence of this peak is in disagreement with the thermodynamics of the models, but produces results similar to those observed in experimental studies of some first-order transition systems, including the colossal MCE. This shows how the odd peaks sometimes observed in some ΔS_M estimations from magnetization measurements may be the product of the data analysis procedure, and should not be immediately interpreted as a consequence of the particular physics of the studied system.

Our results can also help quantify the disagreement between calorimetric and magnetic methods to estimate ΔS_M found in various first-order systems, since the magnetic measurements may not have been performed under equilibrium conditions (visible hysteresis). By using the Landau theory or the mean-field model to experimental (nonequilibrium) data, the equilibrium M versus H curves can be estimated and the true magnetic entropy change can then be calculated. Results from this approach will be published elsewhere.

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