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INTERPRETING AND MODELING MAGNETOCALORIC DATA AND PROPERTIES: THE LANDAU THEORY OF PHASE TRANSITIONS AND MEAN-FIELD THEORY

J.S. AMARAL*, V.S. AMARAL

Departamento de Física and CICECO, Universidade de Aveiro, Campus de Santiago, 3810-193 Aveiro, Portugal

*Corresponding author: *e-mail address*: jamaral@fis.ua.pt

ABSTRACT

We have recently shown [1] how the Landau theory of phase transitions can be used to model magnetocaloric properties of ferromagnets, such as the dependence of ΔS_M in ΔH and T, and studied how the Landau coefficients, related to magnetoelastic coupling and electron spin condensation energy in manganites, and their temperature dependence can be used to interpret the change from 1st- to 2nd-order phase transitions (PT) [2]. A similar application of this method was used in the study of the itinerant electron metamagnetic $La(Fe_{1-x}Si_x)_{13}$ system by Fujita *et al*. [3], where the dependence of the Landau parameters with T reflects the thermal variation of amplitude of spin fluctuations [4]. The insight given by the Landau theory is therefore of extreme value when one wants to understand how the couplings of the studied systems influence a 1st- or 2nd-order PT and the magnetic entropy changes, guiding materials modifications and conditions for optimization. However, the Landau theory is not designed to account for the magnetic behavior up to high fields/ magnetic saturation, since it depends on a power expansion of the order parameter. This limitation can be overcome by using a generalized mean-field analysis of magnetization data, which is also well suited to estimate magnetocaloric properties of materials. By using the general properties of the mean-field model, the mean field exchange field, usually described from $H_{exch.}= \lambda M$, is estimated directly by a scaling method from magnetization data. The generalization proposed does not suppose a constant λ, and instead allows extracting the dependence of λ in M and/or T to account for additional couplings of the magnetization to other degrees of freedom. We show results of this analysis for manganite systems with 1st- and 2nd-order PT, and Tc ranging from 150 to 340 K. This method allows one to analyze the dependence of λ in M and/or T, which would respectively indicate adiabatic magnetoelastic couplings or vibronic coupling proposed for manganites [5]. The analysis of the data in a large temperature and field range allows a suitable interpolation scheme and a consistent study of the magnetic entropy.

INTRODUCTION

Indirectly estimating the magnetocaloric effect by magnetization measurements is straightforward, using the Maxwell relation between magnetization, applied magnetic field, temperature and magnetic entropy (1).

$$\left(\frac{\partial S_M}{\partial H}\right)_T = \left(\frac{\partial M}{\partial T}\right)_H \quad (1)$$

After integration expression (1) yields

$$\Delta S_M(T,\Delta H) = \int_{H_i}^{H_f} dS_M(T,H)_T = \int_{H_i}^{H_f} \left(\frac{\partial M(T,H)}{\partial T} \right) dH \tag{2}$$

This method of estimating the magnetic entropy variation accumulates errors in the magnetic moment and magnetic field upon numerical integration/derivation of experimental data, which is usually taken as isothermal magnetization measurements. Pecharsky and Gschneidner Jr. have shown that this accumulation of experimental errors can be between 20 and 30% [6]. Still, this is the usual method of estimating magnetic entropy variation from magnetization measurements, and in practice, it is used in an approximate form, using sums and discrete differences of data [7], as described in equation 3.

$$\Delta S_M(T,\Delta H) = \sum \frac{(M_n - M_{n+1})}{T_{n+1} - T_n} \Delta H_n \tag{3}$$

where M_n and M_{n+1} are measured magnetization values for the temperatures T_{n+1} and T_n.

Usually, due to the restricted time to obtain data of magnetization as a function of temperature and magnetic field, a limited set of data points is used. This makes difficult an accurate calculation of the entropy due to experimental noise. A more reliable analysis of the data can be devised applying interpolation schemes starting from known theories which also allow a physical interpretation of its parameters.
In a recent work [1] we have used the Landau theory of phase transitions to model the magnetocaloric effect in ferromagnetic materials and study the magnetoelastic coupling influence. In this framework, we used the expansion of magnetic energy (4):

$$G(M,T) = G_0 + \frac{1}{2} A.M^2 + \frac{1}{4} B.M^4 + \frac{1}{6} C.M^6 - MH \tag{4}$$

Here A, B and C are the usual expansion coefficients [8]. From this, after energy minimization, results the magnetic equation of state (5).

$$\frac{H}{M} = A + B.M^2 + C.M^4 \tag{5}$$

The corresponding magnetic entropy is obtained from differentiation of the magnetic part of the free energy with respect to temperature (6):

$$S_M(T,H) = -\frac{1}{2} A'(T) M^2 - \frac{1}{4} B'(T) M^4 - \frac{1}{6} C'(T) M^6 \tag{6}$$

where *A'(T), B'(T)* and *C'(T)* are the temperature derivatives of the expansion coefficients. Expressions (4) and (5) are sufficient for an estimation of the magnetic entropy change under a magnetic field change from 0 to H, $\Delta S_M(T,H)$, as long as the Landau coefficients *A*, *B* and *C* and their dependence in temperature are known. These can be obtained by experimental data analysis of magnetization measurements, as we show in detail in an example of application.

The $La_{0.665}Er_{0.035}Sr_{0.3}MnO_3$ manganite is ferromagnetic, with a second-order magnetic phase transition with $T_C \sim 340$ K. From magnetization data taken from a SQUID magnetometer (up to 5 T applied magnetic field), we plot H/M versus M^2, the isothermal Arrott plots. For each temperature, and within the limits of Landau theory, we fit a 2nd-order polynomial corresponding to equation 5, as shown in Figure 1:

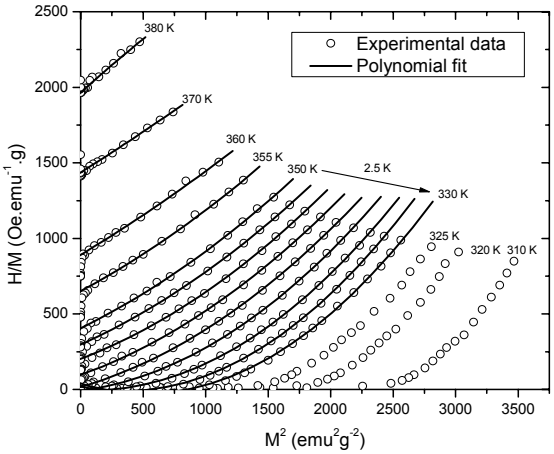

Figure 1: Arrott plots for $La_{0.665}Er_{0.035}Sr_{0.3}MnO_3$, and corresponding 2nd-order polynomial fit for each isothermal curve.

From this fit we obtain the dependence of the Landau parameters *A*, *B* and *C* in the temperature range where Equation 4 is reliable (T > 325 K), as shown in Figures 2, 3 and 4 respectively. Interpolation of data is made by fitting polynomial functions of arbitrary order.

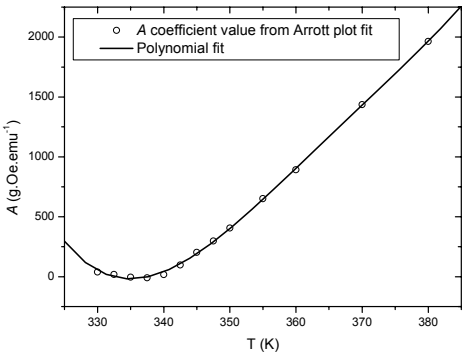

Figure 2: *A* coefficient and corresponding polynomial fit for $La_{0.665}Er_{0.035}Sr_{0.3}MnO_3$.

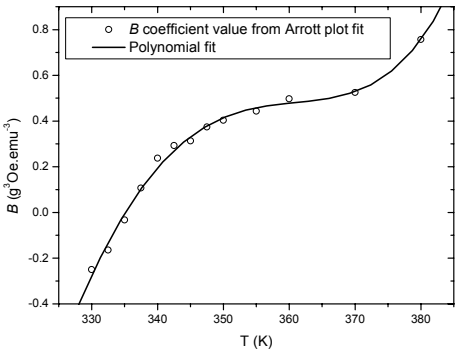

Figure 3: *B* coefficient and corresponding polynomial fit for $La_{0.665}Er_{0.035}Sr_{0.3}MnO_3$.

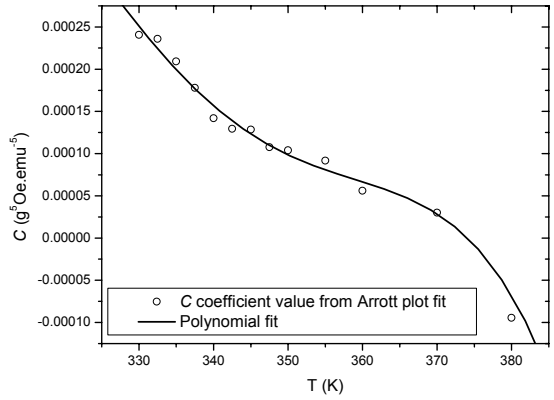

Figure 4: *C* coefficient and corresponding polynomial fit for $La_{0.665}Er_{0.035}Sr_{0.3}MnO_3$.

With *A(T)*, *B(T)* and *C(T)* values, and by using only the magnetic equation of state (5), we can generate isothermal *M* versus *H* plots, which are shown in Figure 5, compared to experimental data. The Landau theory provides a smooth interpolation of the data in the range of validity. The magnetic entropy variation can then be calculated using equation 6, as shown in Figure 6, and compared with the calculation using discrete points from Maxwell relation integration (7).

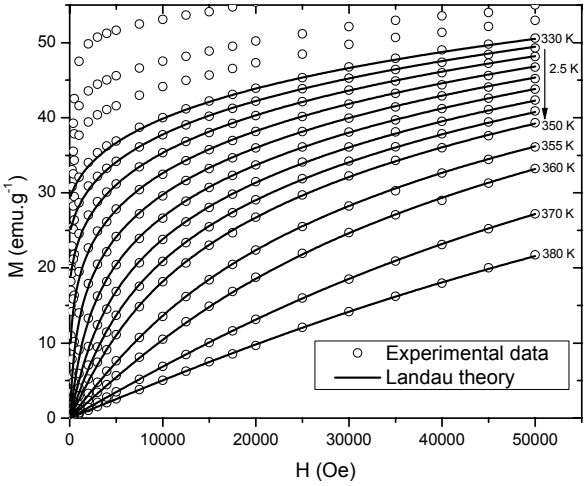

Figure 5: Comparison between experimental magnetization data (open circles) and data obtained from Landau theory (solid lines), for $La_{0.665}Er_{0.035}Sr_{0.3}MnO_3$.

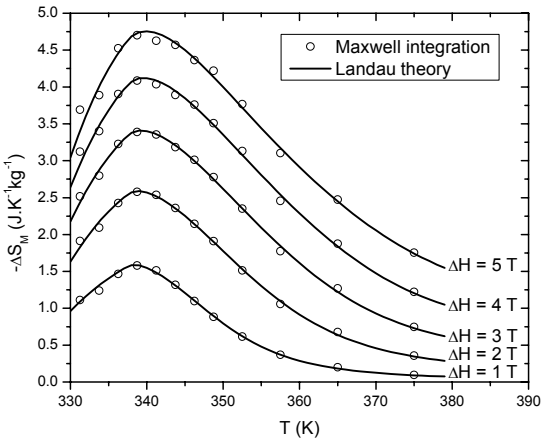

Figure 6: Comparison between magnetic entropy variation from Maxwell integration (open circles) and Landau theory (solid lines), for $La_{0.665}Er_{0.035}Sr_{0.3}MnO_3$.

While this method of estimating magnetic entropy variation is valid, a deeper physical interpretation of the coefficients allows one to further interpret the magnetic system in study. In the case of manganites, the *B* coefficient has been shown to be affected by magnetoelastic coupling as well as the electron condensation energy that occurs in the metal-insulator transition on these compounds [9]. It is then possible to study the impact of these couplings in magnetic entropy variation by calculating ΔS_M curves for several types of *B(T)* dependencies, which can change the magnetic transition from 1st to 2nd order, severely changing its magnetic behavior and properties.

The Landau theory has also been successfully used by Das and Dey in manganite systems [10], and by Fujita and Fukamichi in the itinerant electron metamagnetic $La(Fe_{1-x}Si_x)_{13}$ system (1st order transition and $\Delta S_M \sim 20$ $J.K^{-1}.kg^{-1}$ for 2 T of field variation), where the dependence of the Landau parameters with T reflects the thermal variation of amplitude of spin fluctuations [4].

1 MEAN FIELD ANALYSIS

As is known, the Landau theory cannot account for the magnetic behavior up to high fields/ magnetic saturation, since it relies on a power expansion of the magnetization. This limitation, which becomes important at lower temperatures and high fields, led us to develop a generalized mean-field analysis of magnetization data [submitted for publication], which is also well suited to estimate magnetocaloric properties of materials, that does not start from a conventional fitting of the data using Brillouin functions and fixed molecular field [11].

We describe a ferromagnetic system obeying a general mean-field law, with a general mean-field (molecular) exchange field H_{exch} (usually taken simply as λM):

$$M(H,T) = f\left(\frac{H + H_{exch}}{T}\right) \tag{7}$$

Then if the f function is monotonous (like the Brillouin function in usual modelling), for corresponding values with the same M, the value of $(H + H_{exch})/T$) is also the same, a function k(M):

$$\frac{H + H_{exch}}{T} = k(M) \tag{8}$$

Assuming this, and by taking H and T groups of values for regular M values, one can, using expression (8), plot a graph of H/T versus $1/T$.

$$\frac{H}{T} = k(M) - \frac{H_{exch}}{T} \tag{9}$$

For each M value, the slope equals H_{exch} , which is obtained fitting linear functions to H/T versus $1/T$ plots. This is reliable as long as H_{exch} is only a function of the magnetization M. Figure 7 shows H/T versus $1/T$ plots of the $La_{0.665}Er_{0.035}Sr_{0.3}MnO_3$ system, the same used in the previous section of this text.

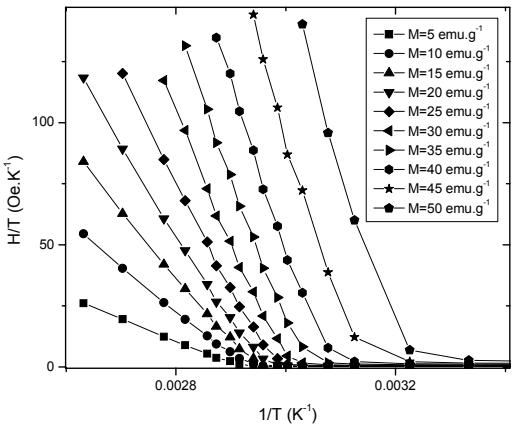

Figure 7: H/T versus $1/T$ plot for $La_{0.665}Er_{0.035}Sr_{0.3}MnO_3$.

Since expressions 7-9 are valid without assuming any particular dependence of exchange field on magnetization, one can verify if this has terms of order higher than linear (eg. $H_{exch}=\lambda M + \lambda_3 M^3$), by plotting the exchange field values for each value of M as shown in Figure 8. With the characterization of the exchange field, the consistency of the analysis is verified by a scaling plot of the experimental data as a function of the scaling variable expression (6): $(H + H_{exch})/T$. The scaling curve represents the f function, which can then be compared to the simple case of a single Brillouin function (or more complex cases).

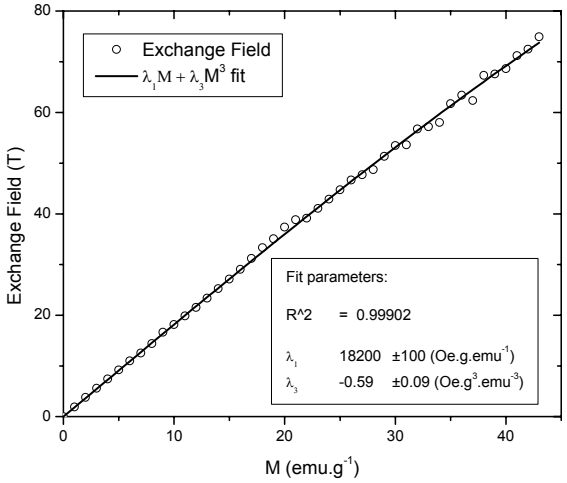

Figure 8: Exchange field and corresponding $\lambda M + \lambda_3 M^3$ fit for $La_{0.665}Er_{0.035}Sr_{0.3}MnO_3$.

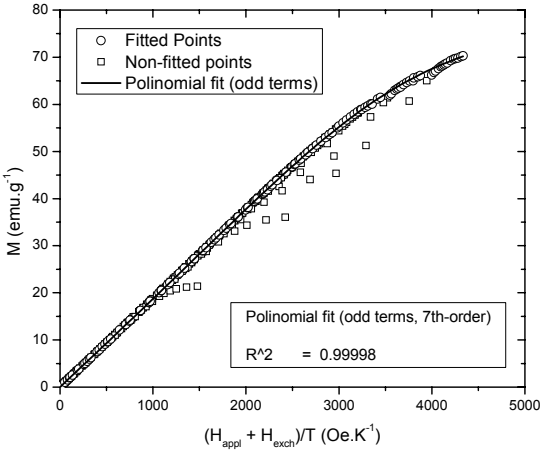

Figure 9: State function, $f((H_{appl} + H_{exch})/T)$, and corresponding fit for $La_{0.665}Er_{0.035}Sr_{0.3}MnO_3$.

With the *f* function and the exchange field determined, it is possible to generate M versus H curves and compare again to experimental data, in a similar fashion to Landau theory results, as shown in Figure 10. The scaling function *f* is directly related to the magnetic entropy through the following thermodynamic relation:

$$f^{-1}(M) = \frac{\partial S_M}{\partial M} \tag{10}$$

Therefore the magnetic entropy variation between an applied field H_1 and H_2 is given by:

$$\Delta S_M = \int_{M|_{H_1}}^{M|_{H_2}} f^{-1} dM \tag{11}$$

Which is equivalent to expression (12), simplifying numerical calculations:

$$\Delta S_M = M|_{H_2} - M|_{H_1} - \int_{x_1}^{x_2} f dx\,, \tag{12}$$

where $x_1 = \frac{H_1 + \lambda M|_{H_1} + \lambda_3 M^3|_{H_1}}{T}$ and $x_2 = \frac{H_1 + \lambda M|_{H_2} + \lambda_3 M^3|_{H_2}}{T}$.

So, integrating using expression 12 and the *f* function from Figure 9, the magnetic entropy variation, for the $La_{0.665}Er_{0.035}Sr_{0.3}MnO_3$ system is obtained, now allowing an interpolation in a broader temperature range than the Landau theory (Figure 11).

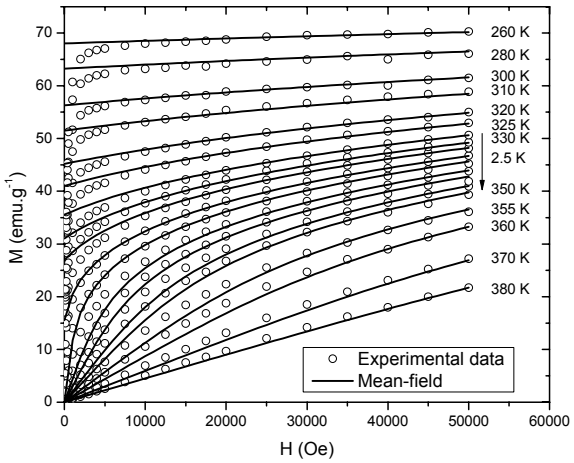

Figure 10: Comparison between experimental Magnetization data (open circles) and data obtained from mean-field analysis as described in the text (solid lines), for $La_{0.665}Er_{0.035}Sr_{0.3}MnO_3$.

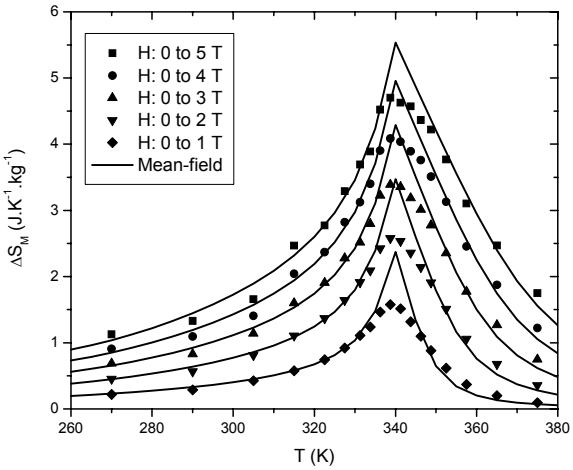

Figure 11: Comparison between magnetic entropy variations estimations by Maxwell relation integration (solid points) for several ΔH values and corresponding solid lines from mean-field method for $La_{0.665}Er_{0.035}Sr_{0.3}MnO_3$.

The described method is also valid for 1st-order magnetic phase transitions, where in similarity with the parameter B in Landau theory, the value of λ_3 in the $H_{exch} = \lambda M + \lambda_3 M^3$ expression changes the order of the phase transition.

Figure 12 and 13 show exchange field and *f* function for the ferromagnetic $La_{0.60}Y_{0.07}Ca_{0.33}MnO_3$ manganite which has a 1st-order magnetic phase transition with a Tc ~ 150 K. Figure 12 clearly shows a strong positive λ_3 dependence, which is in agreement with the 1st-order transition.

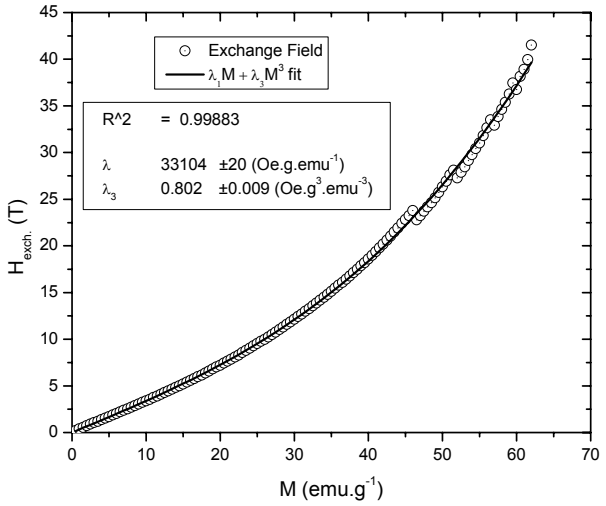

Figure 12: Exchange field and corresponding $\lambda M + \lambda_3 M^3$ fit for $La_{0.60}Y_{0.07}Ca_{0.33}MnO_3$.

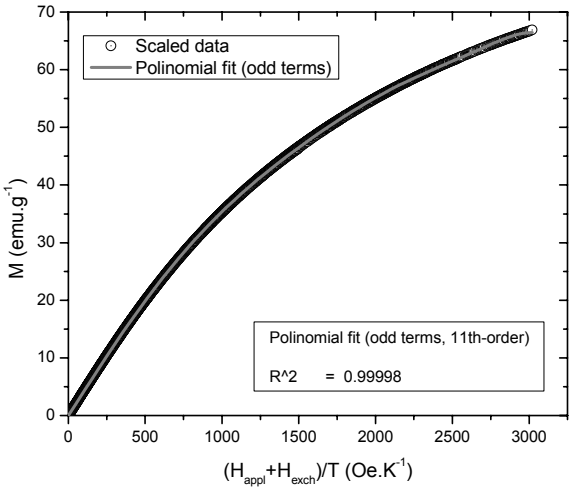

Figure 13: State function, $f((H + H_{exch})/T)$, and corresponding fit for $La_{0.60}Y_{0.07}Ca_{0.33}MnO_3$.

Landau method results for this system are published elsewhere [1].

CONCLUSION

In this work we have shown in detail two methods of estimating magnetic entropy variation with applied magnetic field in ferromagnetic systems, based on the Landau theory of phase transitions and the molecular mean-field model. The analyses of either method allow a deeper study of the magnetic properties of the system, as well as a solid basis for modeling magnetic entropy results.

ACKNOWLEDGEMENTS

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