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# Two different critical regimes enclosed in the Bean–Rodbell model and their implications for the field dependence and universal scaling of the magnetocaloric effect

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In the last few years power laws and universal scaling have been extensively used to study the field dependence of the magnitudes involved in the magnetocaloric effect of materials. They are key tools which allow us to compare the performing properties of different materials regardless of their nature, processing or experimental conditions during measurements. It was proved that power laws and universal scaling are a direct consequence of critical phenomena in the neighborhood of phase transitions. However, there remains some controversy about the reliability of these procedures. In this work we use the well-known Bean–Rodbell model to confirm that these features are unmistakably related to the critical behavior of the continuous phase transitions. In this specific model, universal scaling occurs either at a purely mean field second order transition or at a tricritical point. Finally, we analyze in detail if the universal scaling is compatible with materials at the tricitical point, making a comprehensive comparison with available experimental data from the literature. We conclude that it is really difficult to know with full certainty if a sample really is in the tricritical regime.

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# 1 Introduction

The study of magnetocaloric effect (MCE) has attracted a lot of attention among the scientific and engineering communities in the last few years. This interest arises not only from its potential applications in near room temperature refrigeration but also from other energy conversion matters,<sup>1</sup> and there are convincing arguments to postulate that magnetocaloric materials will perform a crucial role in the upcoming technologies of the near future.<sup>2</sup>

The possibility of building a refrigeration device for near room temperature based only on the application and removal of a magnetic field in the presence of a ferromagnetic substance like gadolinium was firstly proposed by G. V. Brown in 1976.<sup>3</sup> This type of device has two main advantages compared with the rest of the existing refrigeration machines. On the one hand, since the driving force arises from the variation in the applied field, the number of energy consuming elements like power generators, compressors, *etc.* is drastically minimized resulting in an increment of the cooling efficiency, especially if

the magnetic fields are produced using permanent magnets. On the other hand, these devices are very environmentally friendly because they do not use any gaseous substances in the refrigeration process which are normally toxic or responsible for the greenhouse effect. Brown's idea opened the door to a completely new technology which is now under development with a remarkably large number of working prototypes.<sup>4</sup> The research on magnetocaloric materials was clearly increased when giant MCE was discovered in Gd<sub>5</sub>Si<sub>2</sub>Ge<sub>2</sub> at the end of the 90's.<sup>5</sup> Promptly many other materials with an extraordinary MCE were found,<sup>6-9</sup> still today dozens of new materials with a giant MCE are described every year. As a result, hundreds of magnetic materials belonging to different chemical families have been studied and fully characterized<sup>10,11</sup> with valuable information about the most intimate details of the structural and magnetic phase transition, often unveiled with the aid of first principles calculations.<sup>12-16</sup> Moreover, a big effort has been put to improve these applications on refrigeration using other related phenomena like the electrocaloric or barocaloric effects.<sup>17-19</sup>

Due to the huge number of known magnetocaloric materials it was necessary to develop strategies which allow us to compare them in an accurate way regardless of their nature, processing or composition. For this purpose, some magnitudes were proposed like the refrigerant capacity which is a measure of the amount of transferred heat between the cold and hot reservoirs. Another problem was related to the fact that very

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#### Paper

often it was difficult to directly compare experimental data for different materials because the applied fields were different and all the MCE parameters were field-dependent. To overcome this issue it was proposed that MCE quantities have a field dependence which can be described by simple power laws. Firstly it was proven for the peak of the magnetic entropy change<sup>20</sup> and some years later it was extended to most of the MCE related magnitudes.<sup>21</sup> In all cases the exponents of the power laws were given in terms of the usual critical exponents typical for each material. Moreover, the possibility of constructing a normalized master curve for magnetic entropy change was pointed out which brings all curves for different applied fields onto the same one, which is applicable for materials undergoing a second order phase transition. It was proven that the collapse onto the master curve was a consequence of critical phenomena.<sup>22</sup> During the last ten years power laws and the phenomenological curve have been widely used by experimental MCE researchers and it has been successfully tested in many second order phase transition materials exhibiting a remarkable MCE. That includes, among others, transition metal alloy ribbons<sup>23,24</sup> and nanoparticles,<sup>25</sup> Heusler alloys,<sup>26</sup> rare earth based intermetallic compounds,<sup>27,28</sup> amorphous<sup>29,30</sup> and partially crystalline<sup>31</sup> alloys and a wide variety of ceramic materials like manganites,<sup>32,33</sup> cobaltites<sup>34</sup> and other complex perovskites.<sup>35</sup>

In spite of all the cited experimental evidence there are critical voices with respect to the application of power laws and the master curve to MCE data. In a recent work by A. Smith et al.,<sup>36</sup> based on a series of numerical simulations in the Bean-Rodbell model,<sup>37</sup> they argued that power laws are basically incorrect and their application to the study of MCE is a mere misunderstanding. The main foundation of their thesis at this point is that MCE exponents are not field-independent at all, so it would be a mistake to consider them constant along any usual applied field range under experimental conditions. On the other hand, with respect to the master curve they claimed that the collapse of different field curves onto the master one is a simple coincidence due to its inherent peak shape. These discrepancies between the experimental results and the conclusions extracted in the frame of the Bean-Rodbell model must be imperatively clarified. Since there is a copious bibliography - only a minimal part was mentioned above - which supports the use of power laws and critical scaling on MCE we lean towards the possibility that results derived from theoretical models must be in agreement with experimental results. If this is not the case the model should be questioned.

Thus, the aim of this work is to shed new light on the critical phenomena involved in the MCE with particular emphasis on the Bean–Rodbell model. Undoubtedly, the usefulness and reliability of this model cannot be questioned at present because it has been extensively used in the last 50 years with many examples of MCE materials.<sup>38–46</sup> The key point of the model which represents its main advantage is that simply varying a single parameter ( $\eta$ ) both first and second order magnetic phase transitions can be treated. However, this parameter is added under a phenomenological assumption related to a volume change during the transition. Therefore, it could affect other

*a priori* unrelated aspects like critical scaling. Therefore, one must be very cautious when extracting conclusions in the restricted frame of a single model without comparing with other models or more appropriately with experimental data, otherwise the obtained results might not be as general as expected.

For this task we will revisit this well-known and widely used magnetic model in order to analytically show how two very different critical regimes are embedded in it depending on the values of the  $\eta$  parameter. One is typical of mean field theories and the other is found in the limiting region between first and second order phase transitions, which correspond with a tricritical point, which has different critical exponents. Then, by means of numerical calculations we will analyze what is the range of applicability, in terms of the applied field, of the power laws in the Bean–Rodbell model as a function of this  $\eta$  parameter, showing that only for  $\eta \to 0$  and  $\eta \to 1$  – that is, at the purely second order phase transition or at the tricritical point - the critical behavior is retained at levels comparable with experimental conditions. In addition we will study how the master curve behaves for the magnetic entropy change in this model according to different values of  $\eta$ , concluding that there is an unambiguous relationship between the collapse of the master curve and the two different critical regimes observed in the model. Finally we will describe in detail the nature of the tricitical point in the Bean-Rodbell model as well as in a wide selection of materials available in recent literature, which will allow us to extract some conclusions about the critical behavior and power laws in this peculiar kind of material.

## 2 Theory and methods

## 2.1 Scaling behavior of MCE

Before starting the analysis of the scaling behavior and the field dependence of some MCE quantities let us remember that MCE is characterized by the maximum magnetic entropy change and the adiabatic temperature change. The first quantity is defined by the typical expression involving the Maxwell relation as:

$$\Delta S_{\rm M}(T,H) = \mu_0 \int_0^H \left(\frac{\partial M}{\partial T}\right)_{H'} {\rm d} H'. \tag{1}$$

And the second one is defined as:

$$\Delta T_{\rm ad}(T,H) = -\mu_0 \int_0^H \frac{T}{c(T)_{H'}} \left(\frac{\partial M}{\partial T}\right)_{H'} \mathrm{d}H' \tag{2}$$

where  $c(T)_H$  is the constant field specific heat of the material and  $\mu_0$  the vacuum permeability. Both quantities are approximately related near the Curie temperature in the following way:

$$\Delta T_{\rm ad}(T \approx T_{\rm C}, H) \simeq -\frac{T}{c(T_{\rm C})_{H'}} \times \Delta S_{\rm M}(T \approx T_{\rm C}, H).$$
(3)

In this work we will focus only on the maximum magnetic entropy change. Probably the first attempt to describe the field dependence of the maximum magnetic entropy change was made over thirty years ago by Oesterreicher and Parket<sup>47</sup> who showed that  $-\Delta S_{\rm M}(T_{\rm C},H) \propto H^{2/3}$  by expanding in a power series the Brillouin function. This empirical law was widely accepted among the magnetocaloric community. Later Kuz'min<sup>48</sup> added a small negative term independent of H to the expression of Osterreicher and Parker, which arose from spatial inhomogeneities of real ferromagnetic materials. J. Lyubiuna *et al.*,<sup>49</sup> based on Landau expansions, proposed a more complex dependence (including Kuz'min's constant term) as:

$$-\Delta S_{\rm M}(T \approx T_{\rm C}) = A(H + H_0)^{2/3} - AH_0^{2/3} + BH^{4/3}$$
(4)

where *A* and *B* are intrinsic material constants and  $H_0$  is related to Kuz'min's constant term. Similar results were obtained by using other mean field theories like the Green's function formalism developed by P. Álvarez *et al.*<sup>50</sup> In an equivalent way similar relations were derived for the adiabatic temperature change.<sup>51</sup>

Independently of these mean-field approaches, V. Franco *et al.*<sup>20</sup> proposed in 2006 that the field dependence of the magnetic entropy change near  $T_{\rm C}$  is a power law with an exponent *n* related to the critical exponents of the material:

$$n(T_{\rm C}, H) = 1 + \frac{\beta - 1}{\beta + \gamma}.$$
 (5)

Note that n = 2/3 is a particular case of this general expression when we choose the mean-field exponents  $\beta = 1/2$  and  $\gamma = 1$ . It was experimentally shown that materials with critical exponents far from the mean-field approach obeyed this power law. This exponent *n* can be calculated for all temperatures from the magnetic entropy change curves and not only at the critical point using the following expression

$$n(T,H) = \frac{d \log|\Delta S_{\rm M}(T,H)|}{d \log H}.$$
(6)

For a given applied field, the behavior of eqn (6) is as follows. It has a minimum near  $T_{\rm C}$ , (exactly at  $T_{\rm C}$  for the mean-field model) whose value is the one pointed out previously depending on the critical exponents (2/3 in the frame of mean-field theory). For temperatures well above the Curie point, in the paramagnetic region, it reaches the value of 2. In contrast, for temperatures below the phase transition it reaches the value of 1 in the purely ferromagnetic region.<sup>21,52</sup>

It was also possible to construct a normalized entropy change curve that was the same for all values of applied fields, which was initially called a master curve and eventually a universal curve. The collapse of all entropy change curves for different applied fields has been proved to be a consequence of the critical scaling behavior.<sup>22</sup> For magnetic systems near the critical point, a scaling relation between magnetization, applied field and temperature must be fulfilled and it has the form:<sup>53</sup>

$$\frac{H}{M^{\delta}} = f\left(tM^{-1/\beta}\right),\tag{7}$$

where  $\delta$  and  $\beta$  are the critical exponents,  $t \equiv (T - T_{\rm C})/T_{\rm C}$  and f is a scaling function which differs depending on the model or the material. For mean-field models this scaling is fulfilled with  $\delta = 3$  and  $\beta = 1/2$ . The universal curve has been successfully

proved in several materials exhibiting a second order phase transition. However, materials with first order phase transitions do not collapse onto a universal curve and this fact can be used to determine the nature of the phase transition in a given material.<sup>54</sup> In order to construct this phenomenological curve we first normalize the magnetic entropy change dividing by the maximum  $\Delta S_{\rm M} / \Delta S_{\rm M}^{\rm pk}$ . Then we choose two temperatures which must fulfill the following conditions:  $\Delta S_{\rm M}(T_{\rm r1} < T_{\rm C})/$  $\Delta S_{\rm M}^{\rm pk} = \Delta S_{\rm M} (T_{\rm r2} > T_{\rm C}) / \Delta S_{\rm M}^{\rm pk} = h$ , where h < 1 is an arbitrary constant. Although in theory h could be freely selected between 0 and 1, too large a value (reference temperatures chosen too close to the peak temperature) would produce large numerical errors due to the limited number of points - in experimental measurements – which lie in that region. Conversely, if h is too small it implies selecting reference temperatures far from the critical region, where other phenomena could take place. Therefore, values in the range 0.5-0.7 are recommended. Once the two reference temperatures are found we define a new variable  $\theta$  for the temperature axis as:

$$\theta = \begin{cases} -(T - T_{\rm C})/(T_{\rm rl} - T_{\rm C}) & \text{if } T \le T_{\rm C} \\ (T - T_{\rm C})/(T_{\rm r2} - T_{\rm C}) & \text{if } T > T_{\rm C}. \end{cases}$$
(8)

The representation of the different  $\Delta S_{\rm M}(T)$  curves on the  $\Delta S_{\rm M}/\Delta S_{\rm M}^{\rm pk}$  and  $\theta$  axis produces the phenomenological universal curve. It was subsequently proved that the use of two reference temperatures was not necessary, unless there were multiple phases in the sample or the demagnetizing factor was not negligible.<sup>21</sup>

By construction, this universal curve (with a single reference temperature) has a certain constrained nature because all scaled curves pass through two points (0, 1) and (+1, h). In order to avoid naive interpretations it is necessary to go one step beyond when determining how good is the collapse of a group of curves. For  $\theta > 0$ , corresponding to the paramagnetic region, no significant deviations are expected. However, for  $\theta < 0$ , in the purely ferromagnetic region, we do expect a spread in the universal curve when moving away from the critical point due to the saturation in the material magnetization. This is a general feature of the critical scaling of any physical magnitude: if we depart from the critical region, scaling will not be fulfilled. This separation can be due to temperature or due to high magnetic fields which make the materials approach saturation.55 Measuring this spread by a simple visual inspection would be a poor criterion and it leads to misconceptions. For this task it is convenient to define a parameter  $\omega(\%)$  which is a measure of the dispersion of the curves at a certain point of the re-scaled temperature axis. It is defined for a given  $\theta_0$  by the following expression

$$\omega(\%) = \frac{W(\theta_0)}{\Delta S_{\rm M}(\theta_0, H_{\rm max}) / \Delta S_{\rm M}^{\rm pk}(H_{\rm max})} \times 100, \qquad (9)$$

where  $W(\theta_0) = \Delta S_M(\theta_0, H_{\min}) / \Delta S_M^{pk}(H_{\min}) - \Delta S_M(\theta_0, H_{\max}) / \Delta S_M^{pk}(H_{\max})$  is the vertical spread of all curves at a certain re-scaled temperature. If the collapse of all curves were perfect,  $W(\theta_0)$  would be zero and hence  $\omega(\%) = 0$ . This parameter should not

be understood as an absolute magnitude but a relative one which allows us to compare different materials. Also, notice that this comparison is only valid when the same range of applied field is used.

### 2.2 The Bean-Rodbell model

In 1962 Bean and Rodbell proposed a magnetic model to study the first order transition in the MnAs compound.<sup>37,56</sup> It exists in two distinct crystallographic structures, at low and high temperatures the hexagonal NiAs structure is found and for a narrow temperature range, from 313 K to 398 K, the orthorhombic MnP structure prevails.<sup>57</sup> The high temperature transition in the paramagnetic region is of second order. The low temperature transition is a combined structural and ferroparamagnetic transition of first order with a large thermal hysteresis and a remarkably high change in volume at this transition of  $\sim 2.5\%$ .<sup>58</sup> From the cited experimental evidence they suggested that the dependence of the exchange interaction was strongly related to the inter-atomic spacing. This dependence was phenomenologically considered via the dependence of the critical temperature  $T_{\rm C}$  on the volume change in the following way:

$$T_{\rm C} = T_0 \bigg[ 1 + \beta \frac{v - v_0}{v_0} \bigg], \tag{10}$$

where  $(\nu - \nu_0)/\nu_0$  is the cell deformation,  $\beta$  measures the slope of the critical temperature curve on the cell, and  $T_0$  is the magnetic ordering temperature in the absence of deformations. Then they considered the expression for the Gibbs free energy per unit volume of a ferromagnetic system, with an arbitrary angular momentum quantum number *J*, in the frame of the molecular field approximation:

$$G_{v} = -\mu_{0}HM_{s}\sigma - \frac{3}{2}\frac{J}{J+1}Nk_{B}T_{C}\sigma^{2} + P\frac{v-v_{0}}{v_{0}} + \frac{1}{2K}\left[\frac{v-v_{0}}{v_{0}}\right]^{2} - TS_{v},$$
(11)

where the first term on the right arises from the applied field *H*; the second is the exchange term; the third, distortion; the fourth comes from the external pressure *P*; and the last is the entropy term. Here, *N* is the density of dipoles per unit volume, *k*<sub>B</sub> is the Boltzmann constant,  $\mu_0$  is the vacuum permeability, *K* is the compressibility, *T* is the absolute temperature,  $S_v$  is the entropy per unit volume and  $\sigma = M/M_s$  is the normalized magnetization, where  $M_s$  is the saturation magnetization at 0 K which is given by  $M_s = Ng\mu_B J$ , with  $\mu_B$  being the Bohr magneton and *g* the Landé factor. From now on we will neglect the pressure term and all entropy terms except the magnetic contribution. The volume change that minimizes the Gibbs free energy satisfies the following condition:

$$\frac{v - v_0}{v_0} = \frac{3}{2} \frac{J}{J + 1} N k_{\rm B} T_0 K \beta \sigma^2 \tag{12}$$

obtained after substituting  $T_{\rm C}$  in (11) for its expression in (10) and deriving  $G_{\rm v}$  with respect to  $(\nu - \nu_0)/\nu_0$ . Now we can introduce the latter result of (12) in (11) and derive again in

order to minimize the Gibbs free energy, this time with respect to  $\sigma$ . When setting the derivative to zero we obtain the following equation of state:

$$\frac{\partial S_{\rm v}}{\partial \sigma} = \frac{g\mu_0\mu_{\rm B}JH}{k_{\rm B}T} + \frac{3J}{J+1}\frac{T_0}{T}\sigma + \frac{9}{10}\frac{J(2J^2+2J+1)}{(J+1)^3}\frac{T_0}{T}\eta\sigma^3$$
(13)

where  $\eta$  is a parameter given by:

$$\eta = \frac{5J(J+1)}{2J^2 + 2J + 1} N k_{\rm B} T_0 K \beta^2.$$
(14)

Bean and Rodbell proved that in this model this parameter governs the nature of the magnetic phase transition. In the absence of external pressure, for  $0 \le \eta < 1$ , the transition is of second order type, while for  $\eta > 1$ , the transition is purely of first order type. This fact is illustrated in Fig. 1, where magnetization under zero field *vs.* temperature curves for gadolinium are shown for different values of the  $\eta$  parameter. If we want to convert eqn (13) into one with a more friendly appearance we must introduce an analytical form of the magnetic entropy. Since we want to perform a derivative with respect to  $\sigma$ , a very convenient way to express it showing its explicit dependence is as follows:

$$\frac{S_{\rm v}(\sigma)}{Nk_{\rm B}} = \log \frac{\sinh\left[\frac{2J+1}{2J}\mathcal{B}_{J}^{-1}(\sigma)\right]}{\sinh\left[\frac{1}{2J}\mathcal{B}_{J}^{-1}(\sigma)\right]} - \sigma \mathcal{B}_{J}^{-1}(\sigma)$$
(15)

where  $\mathscr{B}_{J}^{-1}(\sigma)$  is the inverse Brillouin function. After some algebraic manipulations it is easy to conclude that:

$$\frac{\partial S_{\mathbf{v}}}{\partial \sigma} = -Nk_{\mathbf{B}}\mathscr{B}_{J}^{-1}(\sigma), \tag{16}$$



**Fig. 1** Magnetization curves calculated for gadolinium using the Bean–Rodbell model for H = 0 for different values of  $\eta$  parameter. For  $\eta < 1$  (solid lines) we find a continuous curve because the phase transition is of second order type. However for  $\eta > 1$  (dashed lines) a discontinuity typical of first order phase transition appears and the Curie temperature is shifted to higher values.

and hence eqn (13) becomes:

$$\sigma = \mathscr{B}_{J} \left[ \frac{g\mu_{0}\mu_{B}JH}{k_{B}T} + \frac{3J}{J+1} \frac{T_{0}}{T} \sigma + \frac{9}{10} \frac{J(2J^{2}+2J+1)}{(J+1)^{3}} \frac{T_{0}}{T} \eta \sigma^{3} \right].$$
(17)

Notice that in this model if  $\eta = 0$  we recover the well-known expression obtained by Weiss.<sup>59</sup> So, this model is equivalent to considering an extra term in the Weiss' molecular field. Instead of having  $H_{\rm eff} = H + \lambda M$ , now we would have  $H_{\rm eff} = H + \lambda M + \lambda_3 M^3$ , where  $\lambda$  is a phenomenological constant related to the transition temperature as

$$\frac{1}{\lambda} = \frac{N\mu_0(g\mu_{\rm B})^2}{3k_{\rm B}T_{\rm C}}J(J+1),$$
(18)

and  $\lambda_3$  is another constant which takes into account the contributions arising from the change in volume and determine the nature (first or second order) of the phase transition. These two parameters,  $\lambda_3$  and  $\eta$ , are related to each other in the following way:

$$\eta = \frac{10}{3} \frac{J^2 (J+1)^2}{2J^2 + 2J + 1} \frac{\lambda_3}{\lambda} (Ng\mu_{\rm B})^2.$$
(19)

Finally, using these new parameters  $\lambda$  and  $\lambda_3$ , eqn (17) can be rewritten in a more compact form as:

$$\frac{M}{M_{\rm s}} = \mathscr{B}_J \left[ \frac{\mu_0 g \mu_{\rm B} J}{k_{\rm B} T} (H + \lambda M + \lambda_3 M^3) \right] = \mathscr{B}_J(x).$$
(20)

According to this model the magnetic entropy per mole (using the gas constant R) can be easily calculated using the following analytical expression:

$$\frac{S(T,H,M)}{R} = \log \frac{\sinh\left(\frac{2J+1}{2J}x\right)}{\sinh\left(\frac{1}{2J}x\right)} - x\mathscr{B}_J(x).$$
(21)

Hence the magnetic entropy change due to the variation of the applied field is given by  $\Delta S_{\rm M} = S_{\rm M}(T,H) - S_{\rm M}(T,0)$ . As we have seen, the Bean-Rodbell model provides a disarmingly simple way to reproduce the magnetothermal response of different materials by choosing the appropriate parameters after some empirical inputs. Accordingly, it has been already used to study the MCE of many materials, especially intermetallic compounds<sup>38-41</sup> but also other materials like manganites<sup>42,45,46</sup> that we will consider later. However, the intrinsic limitations of this model should not be forgotten. Among them, we should be aware that it is a mean-field approximation, so it does not provide information about the real critical exponents of the material. It does not take into account possible couplings between the magnetic contribution to the entropy with its electronic or vibrational counterparts, which sometimes cannot be neglected. And finally, it does not take into account phenomena like the influence of the crystalline electrical field or the magnetic anisotropy.

In this work the magnetic entropy change was calculated using this analytical expression and we have also compared it with the results obtained by differentiating and integrating values of M(T,H) using eqn (1), as is often performed with experimental data. For  $\eta \leq 1$ , we found that discrepancies between both methods are negligible. However, for  $\eta > 1$ , the discontinuity in  $[\partial M/\partial T]_H$  in the neighborhood of the critical point provokes a non-negligible difference at  $T_{\rm C}$ . Therefore, in this last case, eqn (21) must be exclusively used. Throughout this work all simulations were carried out using gadolinium as an archetypical work material with  $T_{\rm C}$  = 293 K,  $\rho$  = 7.90 g cm<sup>-3</sup>,  $M_{\rm s}$  = 1963 kA m<sup>-1</sup>, J = 7/2, and g = 2.<sup>60</sup> The  $\eta$  parameter is varied in the range  $0 \le \eta \le 2$  keeping all other parameters constant. Notice that although we have chosen gadolinium as a work material this fact does not represent any serious drawback or lack of generality. By tuning the parameters  $\lambda$  and  $\lambda_3$  it would be possible to reproduce the magnetothermal response of a wide selection of materials as it has been previously shown in the literature.38-46

# 3 Results and discussion

## 3.1 Two critical regimes

In this section we will show how it is possible to find two clearly different critical regimes in the Bean–Rodbell model depending on the value of the  $\eta$  parameter. If we keep close enough to the phase transition we will see that for  $\eta \rightarrow 0$  we have the typical mean field critical behavior. However, for  $\eta \rightarrow 1$ , where the limit between the first and the second order phase transitions is found, another regime with the characteristic critical exponents of the tricritical point appears. We start from eqn (20)

$$\frac{\mu_0 \mu_{\rm B} g J}{k_{\rm B} T} \left( H + \lambda M + \lambda_3 M^3 \right) = \mathscr{B}_J^{-1} \left( \frac{M}{M_{\rm s}} \right). \tag{22}$$

Note that although it would be the same to deal with the Brillouin function itself instead of its inverse, from a practical point of view it is more convenient to use the inverse function. In the limit of  $M \rightarrow 0$  we can expand in a power series the function  $\mathcal{B}_{J}^{-1}(x)$  as<sup>61</sup>

$$\mathscr{B}_{J}^{-1}(x) \simeq \frac{3J}{J+1} x + \frac{9J(2J^{2}+2J+1)}{10(J+1)^{3}} x^{3} + \frac{27J(88J^{4}+176J^{3}+196J^{2}+108J+27)}{1400(J+1)^{5}} x^{5}.$$
(23)

For this calculation it is necessary to retain up to the cubic term. Now substituting the power expansion into (22) and reordering all terms we arrive at the following expression:

$$\frac{H}{M^3} = \frac{\lambda t}{M^2} + \lambda \frac{3}{10} \frac{T}{T_{\rm C}} \frac{2J^2 + 2J + 1}{(J+1)^2} \frac{1}{M_{\rm s}^2} - \lambda_3.$$
(24)

At this point the scaling relation given in (7) is almost fulfilled but in the second term we have the ratio  $T/T_{\rm C}$ . However, we can considerer that in the proximity of the transition  $T/T_{\rm C} \approx 1$  so this dependence is very weak compared to the first term in which we find *t*. So we can express the equation of state in the form of eqn (7) with  $\beta = 1/2$  and  $\delta = 3$ , as it corresponds with the mean field approximation. Besides, we can express  $\lambda_3$  in terms of the  $\eta$  parameter using eqn (19) and we obtain the following expression:

$$\frac{H}{M^3} = \frac{\lambda t}{M^2} + \lambda \frac{3}{10} \frac{2J^2 + 2J + 1}{(J+1)^2} \frac{1-\eta}{M_s^2}.$$
 (25)

In this expression we recognize that in the Bean–Rodbell model the scaling function is simply f(x) = x + c, with *c* being a constant. In this limit we can study the dependence of the magnetic entropy change as a function of the applied field. We are interested in the dependency at  $T = T_{\rm C}$  so we can calculate the partial derivative evaluated at the transition temperature. It is:

$$\begin{pmatrix} \frac{\partial M}{\partial T} \end{pmatrix}_{H,T=T_{\rm C}} = -\frac{\lambda}{3T_{\rm C}C_{\rm MF}(1-\eta)} M^{-1}$$

$$= \frac{\lambda}{3T_{\rm C}} \frac{H^{-1/3}}{\left[C_{\rm MF}(1-\eta)\right]^{2/3}},$$
(26)

where  $C_{\rm MF} = 3\lambda(2J^2 + 2J + 1)/[10(J + 1)^2M_s^2]$ . And finally if we integrate this expression with respect to the applied field we obtain the change in the magnetic entropy

$$\Delta S_{\rm M}(T_{\rm C}, H) = -\frac{\mu_0 \lambda}{2T_{\rm C}} \left[ \frac{H}{C_{\rm MF}(1-\eta)} \right]^{2/3}.$$
 (27)

Notice that this expression satisfies the condition of  $-\Delta S_{\rm M}(T_{\rm C},H) \propto H^{2/3}$  obtained by Oesterreicher and Parker thirty years ago.<sup>47</sup> It is also in agreement with the expression previously obtained by J. H. Belo, *et al.*<sup>62</sup> for the Bean–Rodbell model with  $\eta = 0$ . In our case an extra factor  $1 - \eta$  appears in the denominator. They showed experimentally that  $-\Delta S_{\rm M}(T_{\rm C},H) \propto (H/T_{\rm C})^{2/3}$ . In our case the ratio  $\lambda/T_{\rm C}$  does not depend on the critical temperature and  $C_{\rm MF} \propto T_{\rm C}$  so we obtain the same behavior for  $\eta \neq 0$ .

Nevertheless, one must be careful when applying this result in the data analysis. First of all, it must not be forgotten that this behavior is only valid in the limit  $T \rightarrow T_{\rm C}$  and  $M \rightarrow 0$ . This means that only for low enough applied fields and in the appropriate range of temperature it is possible to use this approximation. Otherwise we will find significant deviation from this power law behavior. In this general expression we have an additional  $1 - \eta$  factor in the denominator which implies that in the limit  $\eta \rightarrow 1$ , when the transition changes from second to first order type, we find a divergence and the obtained expression is not valid anymore. To avoid this divergence it is necessary to expand the inverse Brillouin function up to the fifth order. This is because for  $\eta = 1$  the  $M^3$  term vanishes and hence the partial derivative of the magnetization goes to infinity. In order to obtain the scaling relation in the limit of  $\eta \rightarrow 1$  we proceed in the same way as before and the new equation of state becomes:

$$\frac{H}{M^5} = \frac{\lambda t}{M^4} + \frac{9\lambda \left(88J^4 + 176J^3 + 196J^2 + 108J + 27\right)}{1400(J+1)^4 M_{\rm s}^4}.$$
 (28)

This is the equivalent expression for  $\eta \rightarrow 1$  as the one derived before in eqn (24) for  $\eta \neq 1$ . But now we find the characteristic behavior of a tricritical point with critical exponents  $\delta = 5$ ,  $\gamma = 1$ and  $\beta = 1/4^{63}$  which are different from those of mean field theory. In this case the partial derivative of magnetization with respect to temperature in a constant field evaluated at  $T_{\rm C}$  becomes:

$$\left(\frac{\partial M}{\partial T}\right)_{H,T=T_{\rm C}} = -\frac{\lambda}{5C_{\rm TCP}T_{\rm C}}M^{-3} = \frac{\lambda}{5T_{\rm C}}\frac{H^{-3/5}}{C_{\rm TCP}^{2/5}},\tag{29}$$

where  $C_{\text{TCP}} = 9\lambda(88J^4 + 176J^3 + 196J^2 + 108J + 27)/[1400(J+1)^4M_s^4]$  is another constant. Substituting this expression the magnetic entropy change becomes:

$$\Delta S_{\rm M}(T_{\rm C},H) = -\frac{\mu_0 \lambda}{2T_{\rm C}} \left(\frac{H}{C_{\rm TCP}}\right)^{2/5}.$$
 (30)

This result is in agreement with the general form of the exponent n given in eqn (5) when the critical exponents of the tricritical point are used.

### 3.2 Influence of $\eta$ on the scaling behavior

In the previous section we have derived the critical behavior of the Bean–Rodbell model. In principle, the field dependence of the maximum magnetic entropy change will be given by eqn (27) and (30) for  $\eta \neq 1$  and  $\eta \rightarrow 1$  respectively. However, those relations are restricted to the limiting case of  $T \rightarrow T_{\rm C}$ . In other words, although this behavior is ensured in the neighborhood of the phase transition, *a priori* we have no idea about the range of validity of those expressions. Of course, we know that for a high enough applied field the critical behavior is lost due to the saturation of the sample magnetization. In order to elucidate this point there is a straightforward way which consists of comparing the results obtained with the power law predictions and the value obtained directly with the model.<sup>55</sup>

In Fig. 2 we have represented the field dependence of the magnetic entropy change peak for different values of the  $\eta$ parameter. In each case two vertical lines indicate the applied field values in which the value of  $\Delta S_M^{pk}$  calculated using the power laws differs by 5% or 8% with respect to the real one obtained with the model. As we previously pointed out, we use the magnetic parameters of gadolinium for all  $\eta$  values including both the first and second order phase transitions. According to the graphics in Fig. 2, for  $\eta = 0$ , it is possible to use the power laws up to applied fields of  $\sim 10$  T as we previously demonstrated.<sup>55</sup> However, for non-zero values of  $\eta$  the range of applicability of the power laws progressively becomes narrower. We see how for  $\eta > 0.2$  even for applied fields lower than 1 T the power laws expressions are not valid anymore, being practically inapplicable for  $\eta = 0.8-0.9$ . An explanation for this fact arises from the addition of the extra term  $\lambda_3 M^3$  in eqn (22). This positive term contributes to an increase in the magnetization under the same conditions of temperature and applied field, as is shown in Fig. 1. The power series expansion of the inverse Brillouin function of eqn (23) is based on the assumption that  $\sigma$ remains small enough near the phase transition. To be more precise, in the case of gadolinium, with J = 7/2 for  $\sigma = 0.4$ , the error in the inverse Brillouin function remains under 1% which is reasonable but for  $\sigma$  = 0.6 the error grows over 5%. Hence, the addition of the phenomenological term of  $\lambda_3$  is responsible for



**Fig. 2** Field dependence of the magnetic entropy change peak for different values of the  $\eta$  parameter. In each case the maximum value obtained with the Bean–Rodbell model is compared with the ideal power laws derived in eqn (27) (black dashed line) for the mean field and (30) (blue dashed line) the tricritical point. When possible two vertical lines indicate the applied field values in which the difference between the power law prediction and the real value of the magnetic entropy change peak is 5% and 8%. Note that only for  $\eta \rightarrow 0$  and  $\eta \rightarrow 1$ , the agreement is very good until applied fields of several *T*.

the lack of scaling behavior when  $0 < \eta < 1$ . As is shown in the graphics of Fig. 2 this lack of scaling behavior occurs gradually. However, for  $\eta = 1$ , the critical scaling behavior is suddenly recovered because it corresponds to the tricritical point governed by eqn (30). Again the range of applicability is around 10 T, which is a broad enough interval. Notice that in this case eqn (27) cannot be used because the cubic term in the power expansion vanishes so only the comparison with eqn (30) is available. The reason why the power law does work for  $\eta = 1$  is simple. In this case the second right hand term (arising from the cubic term of the power expansion) of eqn (25) vanishes. So it is necessary to consider the fifth order term of the power expansion. Hence the accuracy of the approximation by the power expansion series increases, although the values of  $\sigma$ were not so small. But this is a peculiarity of the surroundings of  $\eta = 1$  and is fulfilled only in a very narrow range around it. Otherwise the cubic term will dominate and the fifth order term will be negligible as is shown for  $\eta = 0.9$ . Finally, for  $\eta > 1$  the lack of universality is total. There is not any coincidence between any of the two power laws even in the low field region. Although eqn (27) should be valid for  $\eta > 1$ , the shift of the critical point to higher temperatures makes that  $\sigma$  values remain close to 1 even exactly at  $T_{\rm C}$ , as is shown in the magnetization curves of Fig. 1. Therefore, no critical scaling is observed for first order phase transition materials. This is in clear agreement with recent experimental results on MnFe(P,Si) alloys.<sup>64</sup>

Now, we analyze in detail the field dependence of the exponent n at  $T_{\rm C}$  obtained through eqn (6). Note that this expression gives the so-called local exponent. It is often not possible to use this formula when dealing with experimental data because the resolution in applied field is not sufficient. In



**Fig. 3** Field dependence of exponent *n* in gadolinium for different values of  $\eta$  parameter between 0 and 1. Note that in all cases for high enough applied fields they approximate to zero where a complete saturation regime is reached. However, in the inset, we show how for  $\eta = 0$  and  $\eta = 1$  we find that its values of 2/3 and 2/5 are preserved in the range of 1–10 T which corresponds with the usual working conditions. For higher values these power laws are not valid even for materials with critical point near room temperature.

that case the exponent *n* can be obtained by performing a linear fitting in the logarithmic scale of  $\Delta S_M^{pk}$  *vs. H* dataset. The exponent determined in this way will have a similar behavior to that of the local exponent. In Fig. 3, we have plotted the variation of the local exponent *n* with respect to the applied field for different values of  $\eta$ . We have chosen an extremely wide range of the applied field (up to 1000 T) to demonstrate that for high enough applied fields the local exponent tends to zero for all values of  $\eta$ . This is obviously a consequence of achieving the total saturation on the magnetization in the material. For a high enough applied field, an increment in its magnitude is unable to decrease more the magnetic entropy

#### Paper

because all dipoles are completely parallel to the applied field and hence the theoretical maximum of  $R \log(2J + 1)$  is reached. However, if we focus on more realistic applied ranges where power laws are supposed to be valid, we find those values predicted by eqn (5). In the inset of Fig. 3 we show the field dependence of the exponent *n* in a more restricted applied field range. We see how for  $\eta = 0$ ,  $n \approx 0.66$  and for  $\eta = 1$ ,  $n \approx 0.4$ along the applied fields of 0-10 T where we show that power laws are valid. Alternatively, for other values of  $\eta$  we appreciate a stronger field dependence and it is not possible to assign a reasonable constant (*i.e.* slowly varying) value of n for this applied field range. This is in complete agreement with the results shown in Fig. 2 where we pointed out that power laws were not valid for those values of  $\eta$ . In a recent work<sup>36</sup> this lack of scaling for  $\eta < 1$  was interpreted as a proof of the lack of scaling for second-order phase transition materials. Our point of view is completely different. The exponent n is a true scaling parameter independent of the applied field but only in those conditions in which a critical behavior does exist. According to the results of this section we must distinguish between four different scaling regimes; (i) when  $\eta \to 0$ , a typical mean-field scaling with n = 2/3 is observed according to eqn (27); (ii) for  $0 < \eta < 1$ , the addition of the phenomenological term  $\lambda_3 M^3$  to the model provokes an increment of the magnetization near the transition temperature and therefore the range of applicability of power laws progressively shifts to lower values of applied fields, making them practically useless; (iii) when  $\eta \rightarrow 1$ , we find the main features of a tricritical point which separates first from second order phase transition behaviors but magnetization it still continuous with respect to temperature. This tricritical point corresponds to a distinct critical regime with a characteristic exponent n = 2/5 given by eqn (30) and with a range of applicability of power laws in the range of 1-10 T, similar to the one for  $\eta \to 0$ ; and (iv) for  $\eta > 1$ , a first order phase transition takes place and eqn (27) is not valid anymore and no scaling behavior is observed at all.

#### 3.3 Universal curve in the Bean–Rodbell model

Now we focus our attention on the study of the MCE universal curve behavior with respect to the  $\eta$  parameter. For this task we construct the normalized entropy change curves following the procedure described in Section 2.1 with a single reference in temperature for different values of  $\eta$ . We chose values in the range 0–1.2 in the same way as we did in the previous section. In Fig. 4 we have presented the universal curves of the MCE calculated using the Bean-Rodbell model. In each case we have groups of ten curves corresponding to applied fields between 0.5 and 5 T. Before starting the analysis of these results it is convenient to clarify some aspects of this universal curve in order to avoid misconceptions. Once the temperature is normalized according to eqn (8) we can distinguish between the paramagnetic  $\theta > 0$  and ferromagnetic  $\theta < 0$  regions. In all cases we would expect a perfect collapse in the paramagnetic region where non-ferromagnetic behavior is observed in all cases with independence of  $\eta$ . However, for  $\theta < 0$ , we expect that curves do not collapse when moving far away from the

transition temperature and for very high applied fields. This spread of the curves in the ferromagnetic region could be used to quantify the degree of superposition with the aid of the dispersion given in eqn (9), although we will later show that the ferromagnetic region is not the most appropriate for judging the quality of the collapse of the curves associated with the order of the phase transition. This spread depends on several factors, mainly the normalized temperature. Thus, the dispersion  $\omega(\%)$  is defined for a given  $\theta$ , but it also depends on the applied field and the inhomogeneities, impurities and coexisting phases on the sample. In our case we do not have to worry about the latter factors but it is very important to compare dispersions in groups of curves ranging in the same values of applied fields. It is obvious that for higher applied fields the dispersion will grow. By a simple visual inspection of graphics in Fig. 4 we appreciate how the dispersion in the ferromagnetic region for  $\eta = 0$  is small and it starts to grow with increasing values of  $\eta$ . For  $\eta = 0.2$ , a remarkable worsening of the collapse is observed with respect to the  $\eta = 0$  case. This worsening is enhanced until  $\eta = 0.8$  where it seems to decrease compared with the  $\eta = 0.6$  case. For  $\eta = 0.9$ , the coincidence of the curves continues improving and in fact it looks better than the  $\eta = 0$ case because we are getting close to the tricritical point. For  $\eta = 1$ , the dispersions in the ferromagnetic region abruptly disappears. Therefore two minima of dispersion (in absolute values) are found in the neighborhood of the  $\eta \to 0$  and  $\eta \to 1$ points. These points correspond exactly with those described in the previous section in which power laws and critical scaling were valid in the range of 1–10 T. For  $0 < \eta < 1$ , where the scaling behavior and the applicability of power laws fails even for very low fields, the collapse of the magnetic entropy change curves onto the universal one is far from being acceptable. Finally, for  $\eta > 1$ , where a first order phase transition takes place, we observe characteristic features like the discontinuity near the phase transition and how the peak becomes sharper. However, for  $\eta$  values larger than 1 but close enough we appreciate a remarkable collapse of the curves. For instance, the superposition of curves in the case of  $\eta$  = 1.1 is much more evident than in the case of  $\eta$  = 0.9. Also, note how the ordering of different normalized curves changed from  $\eta < 1$  to  $\eta > 1$ . This order inversion provokes that for values of  $\eta$  slightly above 1, a significant collapse of the curves is observed despite belonging to the first order phase transition region. Of course for higher values of  $\eta$  the breakdown of the universal curve is evident, as expected.

To give a more quantitative description of the behavior explained before we have calculated the dispersion given in eqn (9) which measures the deviation of the different curves from the ideal behavior of the universal curve for several values of  $\eta$  in the range 0–1.2. Its dependence with respect  $\eta$  is presented in Fig. 5. We have calculated the dispersion in two different values of  $\theta_0$  in the ferromagnetic region (-2 and -5) and for  $\theta_0 = +2$  in the paramagnetic region. In both ferromagnetic cases the general tendency is the same. Although for  $\eta = 0$  the dispersion value is acceptable, for  $\eta > 0$  it grows significantly until it reaches again a small value for  $\eta = 1$ .



**Fig. 4** Normalized magnetic entropy change curves for different values of  $\eta$  parameter. Note how only for  $\eta \to 0$  and  $\eta \to 1$  the dispersion of the curve in the ferromagnetic region ( $\theta < 0$ ) is small, while for all other cases the collapse is far from being acceptable.



Fig. 5 Variation of the dispersion in the universal magnetic entropy change curves as a function of the  $\eta$  parameter for three different values of  $\theta_0$ .

A change in its sign is found for values slightly above 1 and hence very small values of dispersion are obtained, but this is something artificial and does not have a particular physical meaning. Again for  $\eta$  well above 1 it increases rapidly moving

away from acceptable values. On the other hand, for  $\theta_0 = +2$ , we obtain complementary information. For  $\eta < 1$ , the lack of universal behavior is caused by the magnetic saturation of the sample. This saturation does not take place for the same field values for  $\theta_0 > 0$ , therefore small values of  $\omega$  are displayed and good overlapping of the curves is observed. As we have shown the increase of  $\eta$  enhances the worsening of universal behavior. However, for  $\eta > 1$ , we do not expect universal scaling at all. The green curve in Fig. 5 clearly reveals how there are no deviations in the paramagnetic region for  $\eta < 1$ , but we find remarkable deviations for  $\eta > 1$  which, of course, are not attributable to the sample saturation but to the inherent behavior of a first-order phase transition. So, by investigating the lack of universal behavior in both regions, ferromagnetic ( $\theta < 0$ ) and paramagnetic ( $\theta > 0$ ), we must distinguish between deviations arising from the working conditions of temperature and applied fields, which are going to appear solely in the ferromagnetic regime of second-order phase transition materials<sup>55</sup> and those

deviations arising from the nature of the phase transitions which can take place even in the paramagnetic region.

Some years ago it was proposed that the collapse onto the universal curve could serve as a criterion to distinguish the nature of the magnetic phase transition.<sup>54</sup> According to our results in the frame of the Bean-Rodbell model this still remains true in the vast majority of cases, but we have to be aware of some limiting examples in which materials undergoing first order phase transitions are close to a continuous phase transition and therefore they exhibit some features of second order phase transitions. This fact was already pointed out in samples of  $MnFeP_{1-x}As_x$ .<sup>65</sup> More recently, G. F. Wang et al. carried out a careful study in another similar compound  $Mn_{2-x}Fe_xP_{0.6}Si_{0.25}Ge_{0.15}$  with x = 0.7, 0.8, 0.9 and  $1.0.^{66,67}$  The latter case is especially significant. Although the nature of transition in this compound is definitely first order due to the observation of thermal hysteresis and according to the wellestablished Banerjee criterion,<sup>68</sup> samples with x = 0.9 and 1.0 apparently undergo a first order phase transition, while for x = 0.7 and 0.8 samples undergo a second order type. In such a peculiar case like this, it is very difficult to determine only by means of magnetic measurements the nature of the phase transition. When they applied the universal scaling criterion in this case they obtained similar results. For x = 0.7, they found a minimal spread in the ferromagnetic region comparable to experimental errors and in the other samples the dispersion in the ferromagnetic region was more appreciable. Therefore, in these cases a simple visual inspection of the universal curve does not provide conclusive information about the nature of the phase transition. However, in most of the cases the collapse onto the universal curve implies a second order phase transition and in all cases its absence is a fingerprint of first order type due to the fact that the system states are historically dependent on the external magnetic field and temperature as a consequence of hysteresis.

### 3.4 Comparison with available experimental data

In the previous sections we have shown the relevance of the tricritical point in the Bean-Rodbell model and how it displays a distinct scaling behavior with critical exponents of  $\beta = 1/4$  and  $\gamma = 1$ . At this point it is convenient to compare the results obtained in the model with real data. In principle, it seems difficult to find materials in such a peculiar state between the first and second order phase transitions. Normally one material belong to only one of the two kinds of phase transitions. However, in some materials it is possible to tune the nature of the phase transitions by carefully changing the composition of the compound. A paradigmatic example of this phenomenon is found in rare earth manganites. They are a very extensive family of inorganic materials constituted by complex manganese oxides of general chemical formula  $R_{1-x}M_xMnO_3$ , where R is a trivalent rare earth element and M is a divalent alkaline ion. In the paramagnetic region they have a cubic perovskite-like crystal structure with MnO<sub>6</sub> octahedra in the corners of the unit cell and R cations in the center. By partially substituting this central rare earth cation it is possible to tailor the magnetic properties of the material including the kind of phase transition. The magnetocaloric properties of some of these manganites are excellent and dozens of these compounds have been fully characterized.<sup>86</sup> With careful experimental control of the synthesis it is possible to determine with a certain accuracy the composition in which the compound is in the limit separating a continuous from a discontinuous phase transition. Probably the first successful attempt to describe this crossover phase transition by means of magnetic and specific heat measurements was made in  $2002^{69}$  in the La<sub>1-x</sub>Ca<sub>x</sub>MnO<sub>3</sub> manganite. At that time the order of the phase transition in that compound was unclear, so starting from some limited experimental evidence some experiments were carried out concluding that for x < 0.4 the compound exhibits a first order phase transition while for x = 0.4 the transition showed that it does not diverge, as expected in a second order, and furthermore the critical exponents are in very good agreement with those of the tricritical point. Nowadays more examples of manganites exhibiting similar behaviors have been found. In Table 1 we have listed a wide selection of magnatocaloric materials which are candidates to be very near to the tricritical point. To find out if a given sample is in the neighborhood of a tricritical point, critical exponents can be used as a fingerprint of this condition. Therefore, in Table 1, we presented the Curie temperature together with the values of  $\beta$  and  $\gamma$ . These critical exponents are obtained experimentally from the modified Arrott plots (MAP)<sup>87</sup> or using the Kouvel-Fisher method (KF).<sup>88</sup> Both methods are well established and are widely used but they can lead to significantly different results; for this reason, the method is specified in each case. At a glance, Table 1 shows some relevant aspects which must be taken into account. For example, if we focus on the La<sub>0.6</sub>Ca<sub>0.4</sub>MnO<sub>3</sub> compound cited before, we see that it has been characterized several times and using different methods. Depending on these circumstances the obtained values of critical exponents can be significantly different. The uncertainties associated with using the MAP or KF in the same sample are around 10%. Moreover, the range of the applied field used to determine the critical exponents can affect the obtained values,<sup>74,81</sup> and the determination of the critical temperature suffers from some uncertainty. This fact indicates that synthesis and processing of samples play a crucial role in their magnetic properties. Therefore these measurements have a limited reproducibility due to several factors like the presence of impurities, minority phases, demagnetizing factors, problems controlling and determining the exact composition, etc.

In Table 1 we present more than a dozen of similar materials which are potential candidates to be near a tricritical point because their critical exponents are close to those values predicted by the theory. However, due to the serious issues mentioned it is practically impossible to ensure with enough certainty if they are indeed exactly at the tricritical point. According to our own results in the Bean–Rodbell model, the tricritical point is located in a very "sharp" region, in our case, for  $\eta$  values very close to 1. This means that minimal alterations in composition or the amount of impurities lead to different behaviors. As an example, in Table 1, we find measurements

Compound	Sample	Space group	Method	$T_{\rm C}$ (K)	β	γ	Ref.
Tricritical mean field			_	_	0.25	1.00	
$La_{0.6}Ca_{0.4}MnO_3$	Polycrystalline	Pnma	MAP	265	$0.25\pm0.03$	$1.03\pm0.05$	69
	Polycrystalline	Pnma	MAP	249	$0.249\pm0.002$	$1.01\pm0.02$	70
	Polycrystalline	Pnma	MAP	268	0.248	0.995	71
	Polycrystalline	Pnma	KF	268	0.287	0.989	71
La <sub>0.7</sub> Ca <sub>0.2</sub> Sr <sub>0.1</sub> MnO <sub>3</sub>	Single crystal	$Pnma \rightarrow R\bar{3}c^a$	KF	289	$0.26\pm0.01$	$1.06\pm0.02$	72
$La_{0.5}Ca_{0.3}Ag_{0.2}MnO_3$	Polycrystalline	Pnma	MAP	262	$0.288\pm0.002$	$0.948\pm0.008$	73
	Polycrystalline	Pnma	KF	262	$0.287\pm0.002$	$0.985\pm0.002$	73
La <sub>0.7</sub> Ca <sub>0.25</sub> Ba <sub>0.05</sub> MnO <sub>3</sub>	Polycrystalline	Pnma	MAP	263	$0.225\pm0.002$	$1.05\pm0.03$	74
La <sub>0.7</sub> Ca <sub>0.225</sub> Ba <sub>0.075</sub> MnO <sub>3</sub>	Polycrystalline	Pnma	MAP	258	$0.216\pm0.005$	$0.97 \pm 0.07$	74
$La_{0.5}Ca_{0.4}Li_{0.1}MnO_3$	Polycrystalline	Pnma	MAP	250	$0.254\pm0.001$	$0.99\pm0.02$	75 and 76
	Polycrystalline	Pnma	KF	250	$0.255\pm0.001$	$0.987\pm0.006$	75 and 76
La <sub>0.7</sub> Ca <sub>0.3</sub> Mn <sub>0.91</sub> Ni <sub>0.09</sub> O <sub>3</sub>	Polycrystalline	Pnma	MAP	199	$0.171\pm0.006$	$0.98\pm0.01$	77
La <sub>0.7</sub> Ca <sub>0.3</sub> Mn <sub>0.88</sub> Ni <sub>0.12</sub> O <sub>3</sub>	Polycrystalline	Pnma	MAP	184	$0.262\pm0.005$	$0.98\pm0.01$	78
La <sub>0.1</sub> Nd <sub>0.6</sub> Sr <sub>0.3</sub> MnO <sub>3</sub>	Polycrystalline	Pmmm <sup>b</sup>	$MAP/KF^{c}$	249	$0.257\pm0.005$	$1.12\pm0.03$	79
$La_{0.67}Pb_{0.33}Mn_{0.94}Co_{0.06}O_{3}$	Polycrystalline	R3c	MAP	324	$0.261\pm0.004$	$1.05\pm0.02$	80
	Polycrystalline	R3c	KF	324	$0.255\pm0.002$	$1.07\pm0.06$	80
$La_{0.67}Pb_{0.33}Mn_{0.97}Co_{0.03}O_{3}$	Polycrystalline	R3c	MAP	345	$0.233\pm0.002$	$1.06\pm0.06$	80
	Polycrystalline	R3c	KF	345	$0.237\pm0.002$	$1.03\pm0.05$	80
$Nd_{0.7}Sr_{0.3}MnO_3$	Polycrystalline	Pmmm	MAP	238	$0.271\pm0.006$	$0.92\pm0.02$	81
	Single crystal	Pmmm	MAP	204	$0.57\pm0.01$	$1.16\pm0.03$	82
Nd <sub>0.66</sub> Sr <sub>0.33</sub> MnO <sub>3</sub>	Polycrystalline	Pmmm	MAP	227	$0.23\pm0.02$	$1.05\pm0.03$	83
$(Nd_{0.93}Y_{0.07})_{0.7}Sr_{0.3}MnO_3$	Polycrystalline	Pmmm	MAP	170	$0.234 \pm 0.004$	$1.04\pm0.02$	81
Sm <sub>0.25</sub> Pr <sub>0.3</sub> Sr <sub>0.45</sub> MnO <sub>3</sub>	Polycrystalline	Pnma	MAP	225	$0.230\pm0.004$	$0.952\pm0.023$	84
	Polycrystalline	Pnma	KF	226	$0.255\pm0.021$	$0.957\pm0.014$	84

 Table 1
 Critical parameters of some representative compounds exhibiting possible tricritical behavior. The method column indicates the experimental procedure to obtain critical exponents using a modified Arrott plot (MAP) or the Kouvel–Fisher method (KF)

<sup>*a*</sup> The system  $La_{0.7}Ca_{0.3-x}Sr_xMnO_3$  is very complex, presenting different crystal structures depending on *x*. See recent work<sup>85</sup> for further details. <sup>*b*</sup> In the original reference they affirm that "All samples are single phase with orthorhombic perovskites structure". So we have assigned the same space group as Nd<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub>. <sup>*c*</sup> Both methods were used, but they did not specify the results for each one.

made by different groups in the compound Nd<sub>1-x</sub>Sr<sub>x</sub>MnO<sub>3</sub> for x = 0.3 and 0.33. Such a slight variation in composition produces results with differences around 10% in Curie temperature and critical exponents. Moreover, the processing of the sample dramatically affects its properties as is shown in the single crystal sample of Nd<sub>1-x</sub>Sr<sub>x</sub>MnO<sub>3</sub>, whose tricritical behaviour fully disappears in contrast with its polycrystalline counterpart. For these reasons, when the universal scaling has been applied to this kind of material, results have not been conclusive. In some cases the values of the *n* exponent at  $T_{\rm C}$  obtained from the fitting of  $\Delta S_{M}^{pk}$  as a function of the applied field differs drastically from the 0.4 value predicted by the theory. Also the field dependence of the local n exponent is much more pronounced than usual. Although this local exponent is very difficult to determine in an accurate way from experimental data, these results suggest that the presence of a tricritical point could also depend on the magnitude of the applied field. Conversely, in other cases the agreement is acceptable. Similar results are obtained when trying to construct the universal curve for the magnetic entropy change. However, a very recent work by T.-L. Phan and coworkers<sup>74</sup> sheds new light on this analysis. They prepared polycrystalline samples of La<sub>0.7</sub>Ca<sub>0.3-x</sub>Ba<sub>x</sub>MnO<sub>3</sub> with  $0 \le x \le 0.1$  by a solid-state reaction. By means of several experimental techniques they were able to determine that for x < 0.05 the phase transition was of first order in the whole range of the applied field studied; for  $0.05 \le x \le 0.075$  the phase transition exhibits a mix of characteristics of both transformations being very close to the tricritical point, especially in the high field region. Finally for x > 0.075 the phase transition

becomes purely second order. Although it would be tricky to determine the nature of the phase transition by only using the universal scaling in such a complex case, when they constructed the universal curves they noticed that in the samples belonging to the first order class the deviations in the ferromagnetic part of the universal curves were non-negligible, especially in the parent sample of La<sub>0.7</sub>Ca<sub>0.3</sub>MnO<sub>3</sub>.<sup>89</sup> For samples with purely second order phase transition a perfect collapse was reported and the same for the samples near the tricritical point although in the latter case the magnetic entropy change peak was sharper. Therefore, it is clear that the applicability of the criterion for determining the order of the phase transition based on scaling to materials in the vicinity of a tricritical point is feasible, but only when the high quality of the experiments allows it. In this case the field dependence of the exponent n at  $T_{\rm C}$  is weak and its value is close to 0.4. A similar behavior in the universal curve has been observed in nanocrystals of La<sub>0.7</sub>Ca<sub>0.25</sub>Ba<sub>0.05</sub>MnO<sub>3</sub>.90

## 4 Conclusions

In this work we have demonstrated analytically that the Bean–Rodbell model accurately reproduces two different critical regimes of continuous phase transitions: a mean field second order and a tricritical point, as well as a first order phase transition. For the continuous cases, a power-law field dependence of the magnetic entropy change peak is found, with exponents n = 2/3 and n = 2/5 for the mean field second order phase and the tricritical point,

respectively. Conversely, no scaling behavior is observed for the latter case as expected. In this model, the phenomenological constant introduced to take into account the change in the volume progressively destroys the scaling behavior in the neighborhood of the critical region, making power laws unusable or practically nonexistent for  $0.2 < \eta < 1$ , despite corresponding to a second-order phase transition. In contrast, for  $\eta \rightarrow 0$  and  $\eta \rightarrow 1$  power laws are valid up to applied fields of ~10 T, as expected in materials with Curie point near room temperature. A similar behaviour has been observed for the universal curve of magnetic entropy change in different critical regimes. The lack of scaling typically produces a spread of the universal curve in the ferromagnetic region, which can also be associated with the magnetic saturation of the sample in second order phase transitions. For weak first order phase transitions a more reliable criterion to determine the order of the phase transition would consider the spread of the curves in the paramagnetic range, as this is not affected by saturation.

On a broader context, our results shed new light on some points which remained unclear. (1) We have confirmed the unequivocal relationship between the critical scaling and the power laws and the collapse of curves for different fields onto the universal one and vice versa. (2) Although it is possible to determine the nature of the phase transition after a quick analysis of the universal curve in the vast majority of cases, we have detected that there are some limiting cases of weak first order phase transitions in which the collapse is also good. For these particular cases, it is not possible to determine the nature of the phase transition by a mere inspection of the universal curve. A more detailed quantitative analysis in needed in these cases, focusing on the paramagnetic regime. And finally (3) we have used literature data for a set of manganites which undergo a continuous phase transition near a tricritical point, evidencing that this tricriticality occurs only at specific conditions that are very difficult to control from an experimental point of view. Although according to the theoretical results presented in this paper power laws and critical scaling should take place, it is very hard to reach such a level of accuracy in the experimental samples. Due to this high specificity, minor deviations from the ideal conditions,  $\eta \neq 1$ in the Bean-Rodbell model, make scaling not necessarily applicable. The presence of impurities or minimal uncertainties in the stoichiometry in the samples, otherwise candidates to have tricritical behaviour, would make scaling difficult in practical terms.

The combination of an extensive analysis of the different critical regimes of the Bean–Rodbell model with the revision of literature data and quantitative determination of the scaling of the magnetocaloric results carried out in this work allows establishing on more solid grounds the applicability limits of the scaling behavior and the universal curve for magnetocaloric data.

# Conflict of interest

The authors declare no competing financial interest.

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