A new method for determining the Curie temperature from magnetocaloric measurements

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Abstract

A new method is proposed for determining the Curie temperature from magnetocaloric measurements. It is based on the field dependence of the magnetic entropy change close to the Curie temperature. The main advantages over other methods are that the obtained temperature is field independent and the process is non-iterative and neither need any fitting procedure nor any previous knowledge of the critical exponents of the transition. The reliability of the method is demonstrated using both simulated and experimental data for pure Ni and Fe-based amorphous alloy.

1. Introduction

The Curie temperature (T_C) is an essential parameter to describe the magnetic behavior close to the ferromagnetic-paramagnetic phase transition. The inaccuracy in the determination of T_C could lead to erroneous interpretation of the data, being especially dramatic at the critical region close to the transition when the critical exponents of the transition are involved. In spite of this, the determination of T_C is not trivial. There are three main methods widely used for determining the T_C of a material from magnetization data. One method approximates T_C by the inflection point of the magnetization vs temperature curves ($M_H(T)$), but the obtained temperature ($T_{inflection}$) is in fact field dependent. However, the applied field is needed to obtain a good signal to noise ratio. On the other hand, the Arrott plot [1] method assumes a mean field theory and, from the linear fit of ($H/M_T(H)$) vs $M_T(H)^2$, T_C is approximated to the temperature at which the corresponding isothermal straight line crosses the origin. This method can be generalized for any set of critical exponents to the so called modified Arrott plot. To do this, the Arrott-Noakes equation of state [2] is used, and T_C can be obtained from the linear fit of $(H/M_T(H))^{1/\gamma}$ vs $M_T(H)^{1/\beta}$ (being γ and β critical exponents corresponding to $\chi \sim t^{-\gamma}$ and $M \sim t^{\beta}$, respectively, where $t=(T-T_C)/T_C$). Analogously to the Arrott plot method, the corresponding isothermal line passes through the origin for $T=T_C$. As a main drawback for this method, the critical exponents must be known and an improper choice of them (e.g. using as a first approximation the usual mean field or Heisenberg values) can seriously affect the obtained value of T_C. Finally, the Kouvel-Fisher method [3] is an iterative procedure based on the previous modified Arrott plot method. This method is also widely used to determine the critical exponents of the material. In this case, the magnetization data (using an initial guess of critical parameters) are represented in a modified Arrott plot. From this plot the spontaneous magnetization and the inverse magnetic susceptibility at zero field (χ_0^{-1}) are obtained from the intercepts of each axis. Subsequently, these magnitudes are used to obtain a new set of critical exponents (β and γ) from the slope of the *X* and *Y* vs temperature plots, respectively, being:

$$X = M_S\left(\frac{\partial M_S}{\partial T}\right)^{-1} = \frac{1}{\beta}(T - T_C) \quad (1)$$

$$Y = \chi_0^{-1}\left(\frac{\partial \chi_0^{-1}}{\partial T}\right)^{-1} = \frac{1}{\gamma}(T - T_C) \quad (2)$$

T_C is obtained as the average intercept of both curves with the temperature axis. This sequence is repeated until the parameters converge to a constant value. This method is not a straightforward one and requires a time consuming careful data analysis.

Alternatively, the magnetocaloric effect (MCE), defined as the temperature change in an adiabatic process (ΔT_{ad}) or as the magnetic entropy change in an isothermal process (ΔS_M) when a magnetic field is applied or removed, has been used also to obtain information about the transformation of the material (e.g. critical exponents) [4]. In a first approximation, the temperature at which $|\Delta S_M|$ is maximum, T_{peak}, can be assumed as the Curie temperature of the material but it has been demonstrated that they are not necessarily coincident with a deviation that is field dependent [5]. In this work, a more accurate determination of T_C is proposed from MCE measurements based on the fact that, for second order phase transition (SOPT) materials, the magnetic entropy change can be expressed as a power law of the form $\Delta S_M(T,H)=a(T)H^{n(T,H)}$. It demonstrated that, independently of the field, the value of the exponent n at the Curie temperature and at the peak temperature are coincident (i.e. $n(T_C,H)=n(T_{peak},H)$). Therefore, after determining T_{peak} from the ΔS_M data, and $n(T_{peak})$ from n data, T_C can be obtained as the temperature below T_{peak} at which $n=n(T_{peak})$.

2. Proposed method

The proposed method is based on scaling laws which are valid close to a SOPT. Magnetization curves scale as [6]:

$$\frac{M}{H^{1/\delta}} = f\left(\frac{t}{H^{1/\Delta}}\right) \quad (3)$$

Where Δ=β+γ, δ=1+γ/β and *f* is the corresponding scaling function. On the other hand, due to the Maxwell relationship, ΔS_M can be expressed as:

$$\Delta S_M(T,H) = \mu_0 \int_0^H \left(\frac{\partial M(T,H)}{\partial T}\right)_H \mathrm{d}H \tag{4}$$

Combining (1) and (2), ΔS_M scales as [7]:

$$\frac{\Delta S_M}{H^{(1-\alpha)/\Delta}} = s\left(\frac{t}{H^{1/\Delta}}\right) \tag{5}$$

Where α=2-β-Δ and *s* is the corresponding scaling function. By considering that ΔS_M follows a power law of the form $\Delta S_M(T,H)=a(T)H^{n(T,H)}$, the exponent *n* can be obtained from equation (5):

$$n = \left(\frac{\partial \ln(\Delta S_M)}{\partial\, lnH}\right)_T = \frac{1-\alpha}{\Delta} - \frac{1}{\Delta}\left(\frac{\partial \ln\big(s(x)\big)}{\partial\, lnx}\right)_{x=\frac{t}{H^{1/\Delta}}} \tag{6}$$

The second term vanishes at $T=T_C$, where $x=0$, and also at $T=T_{peak}$, where $\mathrm{d}s(x)/\mathrm{d}x=0$. Therefore it is demonstrated the equality in which the proposed method is based:

$$n(T_C) = n\big(T_{peak}\big) = \frac{1-\alpha}{\Delta} \tag{7}$$

Therefore, T_C can be obtained from magnetization data following three simple steps:

1. $\Delta S_M(H,T)$ curves must be calculated from the experimental data according to equation (4) close to the transition temperature to determine T_{peak}.
2. $n(T,H)$ curves must be calculated from the experimental data according to equation (6) and evaluated at T_{peak}.
3. The temperature T_{MCE} at which $n(T_{MCE})=n(T_{peak})$ must be found using a linear interpolation. From equation (7) T_{MCE} can be identified as T_C.

It could be claimed that the calculation of MCE curves is needed, although there are tools which seamlessly perform this analysis [8] and are not prone to erroneous identification of the parameters. Meanwhile, for the Arrott plot and Kouvel-Fisher methods, the use of standard

software is not possible and subsequently a deeper data analysis is needed (including the determination of the critical exponents of the material, which is sometimes affected by arbitrary selection criteria from researchers). The experimental measurements are the same for the three methods, obtaining similar temperature resolution for the Arrott plot and the proposed method (due to the temperature step of the experimental data), while increased resolution (due to fitting) is obtained with the Kouvel-Fisher method. In the case of the inflection point method although less experimental data and analysis are needed, the obtained temperature depends strongly on the applied field. As well as for the other described methods, FOPT materials are out of the applicability range of the proposed method. Moreover, for multiphase materials, the applicability of the proposed method should require that the Curie temperatures of the phases were well separated

3. Validation of the procedure

a. Simulated data

As a first step to check the validity of the proposed method, simulated data have been generated using the Arrott-Noakes equation of state [2]:

$$H^{\frac{1}{\gamma}} = a(T - T_C)M^{\frac{1}{\gamma}} + bM^{\frac{1}{\gamma}+\frac{1}{\beta}} \quad (8)$$

using the critical exponents (γ and β) corresponding to both mean field (γ=1 and β=0.5) and Heisenberg (γ=1.388 and β=0.367) models. Typical values of a=1 $Oe^{1/\gamma}K^{-1}$ and b=0.01 $(emu/g)^{-(1/\beta+1/\gamma)}Oe^{1/\gamma}$ and T_C=300 K were used. This empirical equation has been shown as a good approximation to the behavior of a ferromagnetic material in the vicinity of a ferro-paramagnetic phase transition (H~0, t~0) and it has been proven that it can reproduce rather well the T and H dependence of ΔS_M near T_C [9]. The simulations for the proposed method shows for the mean field case, profusely studied by Belov [10,11], that T_{peak} and T_{MCE} are field independent and coincident with T_C as shown in the inset of figure 1. However, for the Heisenberg model T_{peak} varies with the applied magnetic field and coincides with T_C at H=0,

meanwhile T_{MCE} remains constant and equal to T_C as shown in figure 1. This figure also shows the calculated $T_{inflection}$ of the simulated curves. For the mean field case $T_{inflection}$ is field independent and coincident with T_C, for the Heisenberg model it is strongly field dependent, departing from T_C as field increases. This result shows an important advantage of the method proposed here: unlike the inflection point method, the obtained result is field independent, although T_{peak} varies with the applied field for a generic set of critical exponents. Figure 2 shows both $\Delta S_M(T)$ and $n(T)$ simulated curves in the vicinity of the transition using Heisemberg critical exponents and the parameters described above and illustrates the proposed method, using the steps described.

b. Polycrystalline Ni

Besides using simulated results, the proposed method has been tested after applying it to a polycrystalline Nickel sample (purity >99.97%). Magnetic measurements were performed in a LakeShore 7407 Vibrating Sample Magnetometer (VSM) up to 15 kOe. MCE analysis has been done with the help of the magnetocaloric effect analysis program [8]. Figure 3 (a) shows the obtained values for $T_{inflection}$, T_{peak} and $T_{MCE.}$ In this case, it can be observed how $T_{inflection}$ is field dependent departing from 624.7 K and reaching 630.7 K at 15 kOe (evidencing that the critical exponents should differ from mean field values) and T_{peak} does not show significant variation in the studied field range. In this case, the transition is relatively abrupt and with the experimental resolution, T_{peak} and T_C are coincident at 624.7 ±0.5 K. In order to check the absence of field dependence of T_{peak} for Ni, we used the equation of state of Arrott-Noakes with a, b, and Tc extracted from [2], showing that the change of T_{peak} for H=15 kOe is 1.1 K, comparable to the temperature step used in our experiments (1 K). For comparison, T_C of Ni sample was calculated using the modified Arrott-Plot with the parameters given by Arrott and Noakes [2] (figure 4(a)). The experimental data give a value of T_C of 624.7±0.1 K in good agreement with our proposed method based on MCE.

c. Transition metal based amorphous alloy

With the aim of checking the proposed method in samples with broader transitions (e.g. due to a distribution of exchange interactions [12]) and for which T_C and T_{peak} are not coincident, it has been applied to an amorphous alloy of nominal composition $Fe_{62}Cr_{12}Cu_1Nb_3Si_{15.5}B_{6.5}$ prepared by melt spinning. The single phase character of the alloy has been confirmed by the existence of a single magnetic transition temperature in the low field M(T) curves. The amorphicity of the sample has been determined by the absence of crystalline peaks in x-ray diffraction experiments. Figure 3 (b) shows the obtained values for $T_{inflection}$, T_{peak} and T_{MCE}. The same qualitative behavior observed for the simulated data (with critical exponents different to mean field) is obtained. For relatively low fields, a strong field dependence of $T_{inflection}$ can be observed (for 25 Oe, $T_{inflection}$=248±1 K and for 300 Oe, $T_{inflection}$=254±1 K). With respect to the MCE method proposed in this work, although T_{peak} increases as the applied magnetic field increases, the calculated T_{MCE} is field independent, with an average value of 248.1±0.5 K. In the case of selecting a single point in the T_{MCE} curve, a value of 248±1 K could be given for which the error is just half of the temperature step. At low fields (below 3 kOe), the measurements do not have a good resolution and the exponent n varies artificially. It is worth mentioning that this is not a limitation of the proposed method as the result is field independent and the value of T_C can be obtained at higher fields where the signal to noise ratio is enhanced.

The obtained value for T_C using the proposed method has also been compared to the results from the Arrott plot and Kouvel-Fisher methods. Using the Arrott plot method, which assumes the critical exponents of mean field (γ=1 and β=0.5), an erroneous value of T_C = 263±1 K is obtained. If we assume the critical exponents of the Heisenberg model (γ=1.388 and β=0.367) in a modified Arrott plot, an improved value of T_C=255±1 K is obtained. Another possibility is to perform a linear fitting of $M^{1/\beta}$ vs T at low fields, being T_C the temperature at which the magnetization becomes zero. Using this method for a field of 25 Oe, T_C =251.4±0.2 K and 250.2±0.2 K for mean field and Heisenberg exponents are obtained, respectively. From these

results, it can be observed that the choice of the critical exponents strongly affects the value of T_C obtained from this method.

In the case of the Kouvel-Fisher method, the inset of figure 4 (b) shows the obtained $X=Ms(\mathrm{d}Ms/\mathrm{d}T)^{-1}$ and $Y=\chi_0^{-1}(\mathrm{d}\chi_0^{-1}/\mathrm{d}T)^{-1}$ vs temperature plots after a sufficient number of iterations (around 15) in order to reach convergence. The values of β=0.43±0.02, γ=1.67±0.18 and T_C=249.6±0.3 K are obtained. The modified Arrott plot with the obtained parameters is shown in figure 4 (b) to evidence the good agreement with the Arrott-Noakes equation of state using these parameters. It is worth mentioning the time consuming analysis needed to obtain this final value of T_C using this method. However, our proposed method does not require neither an iterative procedure nor a fitting (beyond just a linear interpolation to obtain $n(T_{MCE})=n(T_{peak})$).

4. Conclusions

In conclusion, a new method for determining the Curie temperature from magnetocaloric measurements of SOPT materials has been proposed. Its validity has been checked using simulations and experimental measurements on a polycrystalline Ni sample and Fe-based amorphous alloy. The method is based on the equality of the field dependence of magnetic entropy change at the Curie temperature and at the temperature for which the magnetic entropy change is maximum. The main advantages of the proposed method are:

-The obtained temperature is field independent.

-It is not necessary neither an iterative nor a fitting procedure.

-No assumptions on the critical exponents describing the transition are required.

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Figure Captions:

Figure 1: $T_{inflection}$, T_{peak} and T_{MCE} obtained for simulated data using Arrott-Noakes equation of state with critical exponents of mean field (inset), for which the three values coincide, and Heisenberg model (main panel).

Figure 2: Simulated $\Delta S_M(T)$ for H=15 kOe and $n(T)$ curves for H=5, 10 and 15 kOe to evidence although T_{peak} depends on H, T_C is field independent.

Figure 3: $T_{inflection}$, T_{peak} and T_{MCE} obtained from the experimental data of Ni (a) and the Fe-based amorphous alloy (b).

Figure 4: Modified Arrott plots with the parameters obtained from [2] for the Ni sample (a) and the Kouvel-Fisher method after convergence for the Fe-based amorphous alloy (b). **Inset**: $Ms(dMs/dT)^{-1}$ and $\chi_0^{-1}(d\chi_0^{-1}/dT)^{-1}$ vs T plots.

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