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A unified approach to describe the thermal and magnetic hysteresis in Heusler alloys

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Different excitations, like temperature, magnetic field, or pressure, can drive a martensitic transition in Heusler alloys. Coupled phenomena in these materials lead to interesting magnetocaloric and barocaloric effects ascribed to this transition. In this work, we demonstrate that isothermal transformations induced by a magnetic field and isofield transformations induced by the temperature can be described using the same framework. By defining an effective temperature that relates field and temperature through the properties of the system (magnetic moment and entropy of the transition), both kinds of loops can be transformed into the other kind, therefore providing a more effective way of characterizing hysteretic samples. The validity of this effective temperature approach to describe the transition holds for martensite to austenite transformations as well as reversal ones, and thus, the hysteresis phenomena can be described using this single general excitation. *Published by AIP Publishing.* [http://dx.doi.org/10.1063/1.4963319]

Ground energy level identifies the state and structure of a physical system in the thermodynamical equilibrium. However, exciting the system can lead to a change in the ground state level and induce a transition to a new structure (overcoming an energy barrier) corresponding to the new conditions. When the system is sensitive to different excitations, it is possible to induce this transition in different ways (e.g., temperature, pressure, magnetic field, electric field, etc.). In this sense, Heusler alloys undergo a martensitic transformation from a low temperature and lower symmetry martensite phase to a high temperature and higher symmetry austenite phase. The transition can be driven by changes in temperature or pressure[1] or, in some cases, by application of a magnetic field.[2] This transition in Heusler alloys can be tuned close to room temperature and implies changes in magnetization and volume that leads to giant magnetocaloric[3] and barocaloric effects.[4]

The characterization of the hysteretic phenomena associated with the different excitations is not equally simple or effective. For temperature excitations, magnetization vs. temperature loops take long experimental times due to the required stabilization of the temperature between the different processes. On the other hand, magnetization vs. magnetic field loops are registered in a much quicker way, as field stabilization is usually faster. Recently, it has been proposed to perform first order reversal curve (FORC) analysis of the thermomagnetic hysteresis loops of magnetocaloric materials, which enables a more detailed description of the hysteretic transition, although the technique is limited by the large acquisition time of each FORC.[5] A more detailed characterization, that up to now has been proven prohibitively expensive in terms of time and resources, would allow us to gain a deeper knowledge of the physics driving the transition of these samples. The aim of this work is to provide a theoretical framework, which enables us to characterize hysteretic transitions in a more streamlined way by using a generalized excitation parameter.

The transition temperature in Heusler type alloys can be shifted by applying a magnetic field, and the dependence is almost linear.[6] This was used to develop a transition model for simulating the adiabatic temperature change.[6] The identical effects on the transition driven by temperature or magnetic field have been already pointed by Shamberger and Ohuchi[7] and Basso *et al.*[8] In the former paper, the authors proposed, for a given temperature between martensite start (Ms) temperature and austenite start (As) temperatures, an equivalency between a temperature change (ΔT) and a magnetic field change ($\mu_0 \Delta H$) of the form $\Delta T \Delta S = \mu_0 \Delta H \Delta M$, which assumes that the changes in entropy (ΔS) and magnetization (ΔM) ascribed to the transition are independent of the temperature and magnetic field (see Eq. (9) in Ref. 7). This means that, using the Clausius-Clapeyron equation, these authors could relate the partial transformations caused by temperature to the partial transformation curves caused by a field increment at a temperature, which corresponds to the center of the temperature hysteresis loop. In the second paper, Basso *et al.* used the difference between the Gibbs free energies of the martensite and the austenite phases as a single parameter to describe the transition. This parameter depends on both the temperature and magnetic field. In the present work, the diverse excitations (temperature and magnetic field) driving the martensitic transition of a Ni-Mn-In-Co Heusler alloy with the giant magnetocaloric effect[9] are considered through an effective temperature, T^*, which depends on the magnetic moment and the entropy of the transition. Unlike the previous models, this phenomenological approach simplifies the picture of the transition with a

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simple and intuitive parameter to describe it, not only giving a common description for the effect of a field and a temperature change in the interval at which the transformation is induced but also providing an absolute scale to predict the behavior of the transformation curves above and below the temperature of the experiment. In this letter, we show that this effective temperature approach allows us to rescale both the reversal transformation as well as transformation hysteresis loops of the transitions under different conditions onto a common behavior.

The sample used in this study was a Heusler alloy with $Ni_{45.7}Mn_{36.6}In_{13.5}Co_{4.2}$ stoichiometry prepared by arc-melting and subsequent annealing in a quartz tube at 1173 K for 24 h, under 0.5 bar argon atmosphere, followed by water quenching. Both isofield (from 220 to 310 K, at a heating rate of 2 K/min) and isothermal (up to 5 T, with a field change rate of 4 mT/s) magnetization measurements were performed in the vibrating sample magnetometer option of a Physical Property Measurement System. All the measurements were performed without removing the sample from the quartz holder to avoid any effect of changes in the positioning.

Figure 1(a) shows martensite to austenite (and reverse transitions) isothermal transformations (with a step of 2 K between two consecutive curves) during which the magnetic field was increased up to 5 T and then removed down to 0 T. Between isothermal experiments, the sample was cooled down to 220 K in zero field in order to erase the memory of the transformation. Above 244 K, the austenite phase starts to form for magnetic fields below 5 T. An almost complete transformation can be observed above 256 K in this field range. The reverse transformation (after removing the field) shows a hysteretic behavior being the austenite phase practically arrested for temperatures above 282 K and the martensite phase can no longer be detected above 292 K.

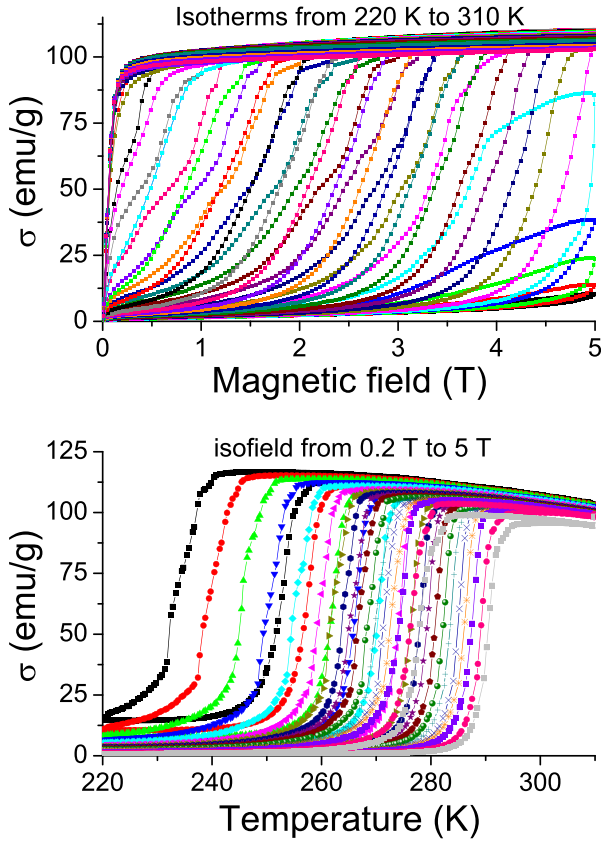

FIG. 1. Isothermal curves (upper panel) and isofield curves (lower panel)

In the case of isofield curves (Fig. 1(b)), the transformation shifts to lower temperatures as magnetic field increases. Hysteretic behavior is also observed in the transformations induced by temperature. In the case of the studied alloy, the martensite phase has a very low Curie temperature (~50 K), and thus, its contribution to the magnetization can be neglected with respect to that of the austenite phase (with a Curie temperature of 398 K).[10] Therefore, in order to estimate the transformed fraction of the austenite phase, X, we can assume that the magnetization is proportional to the amount of the austenite phase. However, magnetization of the pure austenite phase depends on both field and temperature. We have estimated the temperature dependence of the specific magnetization of a pure austenite phase, σ_{Aus}, after fitting a region at which a pure austenite phase exists. This region of pure austenitic response corresponds to the reversible magnetization observed during cooling at $H_{max} = 5$ T from 310 K down to 285 K. This lower limit corresponds to the temperature at which the cooling curve deviates from the heating one (see the inset of Figure s1 in the supplementary material) and assures the absence of transformation in the region to be fitted. Therefore, in this range, σ_{Aus} has been fitted using the following equation:

$$\sigma_{Aus}(T, H_{\max}) = \sigma_S \left(1 - \frac{T}{T_C}\right)^{\beta}, \tag{1}$$

resulting in $\sigma_S = 164$ emu/g, $\beta = 0.306$, and $T_C = 397$ K, in good agreement with the experimental Curie temperature of the austenite phase. The fitting curve was extrapolated to the whole explored temperature range, and the fraction of the austenite phase is then obtained as

$$X = \frac{\sigma_{\exp}(T, H)}{\sigma_{Aus}(T, H_{\max}) f(H)}, \tag{2}$$

where σ_{exp} is the experimental specific magnetization, depending on temperature and field, and f is a field dependent factor, which takes into account that the magnetization of the pure austenite has been estimated only for the maximum applied field. As a first approximation, this factor has been considered temperature independent and is calculated as

$$f(H) = \frac{\sigma_{\exp}(310\,\mathrm{K}, H)}{\sigma_{Aus}(310\,\mathrm{K}, H_{max})}, \tag{3}$$

i.e., the ratio between the specific magnetization values at 310 K (maximum explored temperature) at a field H and at the maximum studied field $H_{max} = 5$ T. It is worth noticing that this rough approach to determine f should be less valid for low fields, and thus, data obtained below 0.5 T are discarded for the analysis. Therefore, using Eq. (2), we can obtain the plots of X vs. temperature and field shown in Figures 2(a) and 2(b).

As it has been shown, the transition from martensite to austenite can be driven either by an increase of temperature or by an increase of magnetic field. Both excitations provide

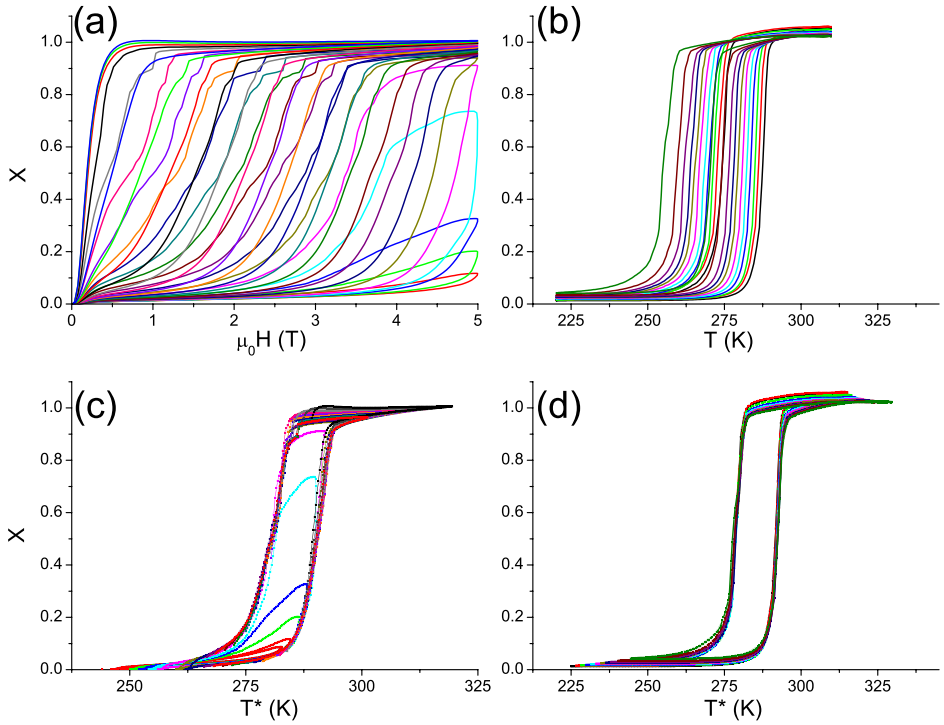

FIG. 2. Transformation curves plotted as a function of both the experimental parameter (field H (a) or temperature T (b)) and the effective temperature T^* ((c) and (d) from (a) and (b), respectively). When represented as a function of T^*, the curves rescale to a common behavior.

energy (thermal or magnetic) to the system, producing the change of structure. Therefore, in order to find the general character of the transition, we propose a phenomenological effective temperature based on the combined effect of both types of energies: thermal and magnetic. What we propose is that the energy of the system, expressed as the thermal energy associated with an effective temperature, is composed of the thermal energy related to the temperature of the sample and the magnetic energy, which allows us to define the effective temperature as

$$T^* = T + \frac{N_A m_S}{M \Delta S_{str}} \mu_0 H, \tag{4}$$

where μ_0 is the magnetic permeability of vacuum, N_A is the Avogadro constant, M is the molar mass, m_S is the saturation magnetic moment per atom and depends on temperature (it has been obtained from the magnetization fitting curve at 5 T), and ΔS_{tr} is the entropy change of the transition per unit mass. The second term on the right hand side of Eq. (4) is formally equivalent to the Clausius-Clapeyron equation, in the sense that the latter relates a shift of the transition temperature to an applied magnetic field. However, in our approach, we are considering T^* as an effective temperature of the system (i.e., a single parameter to describe the whole transformation regardless of the real excitation that drives it), not just a description of the transition temperature. This approach is analogous to previous phenomenological models applied to completely different complex phenomena, like the superparamagnetic transition of dipolarly interacting superparamagnetic particles, in which an effective temperature, related to the energy of magnetic dipolar interactions, was introduced to reproduce the temperature dependence of the hysteretic behavior.[11–13] It is worth noticing that the definition of T^* introduced in expression (4) has no free parameter and depends only on the two excitations involved (field and temperature) and on the properties of the material (magnetic moment and entropy change of the transition). The former property, as described above, has been obtained from fitting the magnetization of the pure austenite phase, while ΔS_{tr} will be obtained from the field dependence of the transition, as will be shown below. Liu *et al.*[6] previously considered the effect of magnetic field to shift the temperature of the transition. They used a linear relationship between the transition temperature and the applied field to develop a transition model for simulating the adiabatic temperature change. In the model proposed here, the proportionality factor is explicitly linked to the properties of the sample in Eq. (4), which allows us to rescale the temperature and field hysteresis loops onto loops, which are formally equivalent.

In order to find the value of ΔS_{tr}, we assume that the point at which the transformation rate is maximum corresponds to a characteristic point of the transition, which should correspond to the same T^* value, regardless of the type of excitation. Eq. (4) predicts a linear trend for both the values of magnetic field at which dX/dH is maximum for each isothermal curve and for the values of temperatures at which dX/dT is maximum for isofield curves. After fitting them to straight lines, the results of both independent plots are in good agreement, resulting in $\Delta S_{tr} \sim 16\,\mathrm{J\,kg^{-1}\,K^{-1}}$ ($1\,\mathrm{J\,mol^{-1}\,K^{-1}}$) (see Figure s2 in supplementary material). Moreover, $T^* = 292\,\mathrm{K}$ at maximum transformation rate, derived from the intercept with the axis, which can be considered as the temperature of maximum transformation rate in the absence of magnetic field.

In order to check the validity of the definition of the effective temperature as the single parameter driving the transition, we represent the transformed fractions as a function of T^* for both isofield and isothermal curves (shown in Figures 2(c) and 2(d)). All the curves collapse to a common behavior. Moreover, it is worth mentioning that both transitions from martensite to austenite (heating or applying field

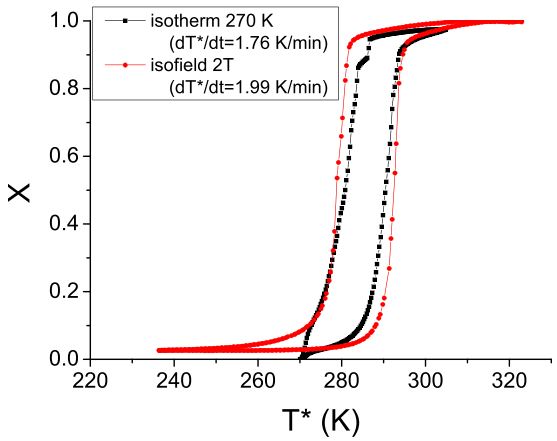

FIG. 3. Comparison of the results obtained from isofield and isotherm experiments as a function of T^*. The higher effective heating rate in isofield experiment shifts the martensite to austenite transition to higher effective temperatures and the reversal transformation to lower effective temperatures, increasing the hysteresis, with respect to the isothermal experiment.

curves) and the reversal transformations from austenite to martensite (cooling or removing field curves) also rescale to a common behavior and thus the hysteresis phenomenon also follows this effective temperature approach. It has to be noted that there are two main limitations for this analysis: (a) for the isofield curves obtained at low fields ($\mu_0 H < 0.5$ T), the simple definition of f loses its validity and (b) for cases with a non-negligible initial fraction of the austenite phase, also discarded for the analysis as martensitic transformation depends on this parameter.[14]

In order to compare the results obtained from isothermal and isofield experiments, Figure 3 shows one example of each type of experiment as a function of T^*. It can be observed that the isothermal experiment exhibits a slightly smaller hysteresis and this can be justified by the faster change of the effective temperature in isothermal experiments ($\mu_0 dH/dt = 4$ mT/s leading to $dT^*/dt = 1.76$ K/min) than for isofield experiments ($dT/dt = dT^*/dt = 1.99$ K/min), which is imposed by the experimental setup.

Finally, it is known that the temperatures describing the martensite transformation: start martensite, Ms, finish martensite, Mf, start austenite, As, and finish austenite, Af, shift to higher values in the presence of a magnetic field. The field dependence of all these temperatures disappears when they are transformed to effective values ($Ms^* = 281 \pm 1$ K, $Mf^* = 275 \pm 1$ K, $As^* = 290 \pm 1$ K, and $Af^* = 294 \pm 1$ K), evidencing that the transition is well described by our effective temperature approach (see Figure s3 in supplementary material). Therefore, a single excitation parameter, here named the effective temperature defined in Eq. (4), is just needed to describe the martensitic transformation.

It is worth mentioning that, although Eq. (4) considers a linear contribution of field to the effective temperature, this is only a first order approach. A finer fitting of Figs. s2 and s3(a) in supplementary material could be done using a power law up to second order in field. However, this higher order coefficient is, in all cases, at least one order of magnitude smaller that the first order coefficient used here, which makes this finer approach an unnecessary complication for the range of fields used in this study. Nevertheless, for larger fields, the nonlinearity should be taken into account, as in Ref. 10.

In conclusion, it has been shown that hysteresis phenomena in systems for which the transition can be driven by different excitations can be described using a generalized effective excitation parameter by means of a phenomenological approach that uses no free parameters. In this paper, both thermal and magnetic hysteresis of a martensitic transformation are described in terms of an effective temperature. Representation of the transformation as a function of the effective temperature allows the collapse of the temperature and field driven transitions in a common curve. Hysteresis loops are also reproduced independently of the type of excitation driving the transition. Unlike previous studies that linked temperature and field at characteristic transition points, we propose the equivalent temperature as a single parameter that allows describing the complete transformation. This opens a way to perform more efficient characterization of these multi-excitation hysteretic systems, facilitating the extraction of finer details of the transformation phenomena (e.g., increasing the effectiveness of measurements for FORC analysis using M-H curves instead of much slower M-T curves, application of well tested single parameter kinetic models to these systems, or optimization of measuring protocols in order to erase thermal history of the system).

See supplementary material for additional figures including the fitting of magnetization curves, temperature and field dependencies of the maximum transformation rates, and effective transformation temperatures.

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