Magnetic Hysteresis

First-Order Reversal Curve (FORC) Analysis of Magnetocaloric Heusler-Type Alloys

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Abstract—The thermomagnetic hysteresis loops of a $Ni_{45.7}Mn_{36.6}In_{13.5}Co_{4.2}$ Heusler-type alloy exhibiting inverse magnetocaloric effect were studied with the help of first-order reversal curves (FORC). These have been measured using two different protocols (either upon heating or cooling the sample) and using different applied magnetic fields. For proper comparison, FORC distributions were shifted according to the field dependent center of the $M(T)$ hysteresis loop, which follows a linear trend. The qualitative behavior of FORC distributions remains the same, allowing their use for fingerprinting the transition, while there is a shift of their maxima along the hysteretic temperature axis and their distributions also get broader along the interaction temperature axis with increasing magnetic field. This was evidence that FORC distributions are dependent on the intensive variables temperature and field. As a consequence, it is necessary to obtain them for different temperatures and fields in order to accurately model the transition.

Index Terms—Magnetic hysteresis, first-order reversal curves, Heusler alloys, magnetocaloric effect.

I. INTRODUCTION

The magnetocaloric effect (MCE) and its application for magnetic refrigeration are attracting increasing interest in the recent years due to energy efficiency and environmental friendliness considerations [Franco 2012, Gutfleisch 2011].

The simplest classification of magnetocaloric materials is by looking at the order of the underlying phase transition. For second-order phase transition materials (SOPT), the gradual change of magnetization with temperature gives rise to a magnetic entropy change peak which, in most of the cases, is of modest magnitude. However, the nature of the transition implies that there is no thermal hysteresis, which is a desirable characteristic for their industrial application as magnetic refrigerants. On the other hand, the abrupt change of magnetization associated with first-order phase transition materials (FOPT) produces a much larger (giant) magnetocaloric effect [Pecharsky 1997], which induces thermal hysteresis, large latent heat, and possibly some time dependencies. Moreover, even if the quasi-static response of some of these FOPT materials is outstanding, there are compositions which can lose some of their efficiency when they are operated in cyclic excitation conditions similar to those which would be used in the refrigeration applications [Kaeswurm 2016]. Therefore, the search for an optimal magnetic refrigerant material aims at identifying compounds or alloys which present a large change in the magnetic entropy, like an FOPT, without the drawback of hysteresis or reduced performance under cyclic conditions, like a SOPT, i.e., a material which is at the tricritical point. Consequently, it is of the utmost importance to be able to fully understand the kinetics of the phase transition in FOPT alloys and compounds in order to be able to predict their behavior under cycling and to identify ways in which the composition or the microstructure could be altered in order to optimize the usable magnetocaloric response of these samples and the way in which stimuli are applied.

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First-order reversal curve (FORC) analysis was initially proposed as a method to identify the Preisach model parameters [Mayergoyz 1986] and was later extended as a model-independent technique to characterize the hysteresis in the magnetization reversals of the magnetic materials [Pike 1999]. Subsequently, it has been proven as a useful technique to model the behavior of hysteretic materials, with examples ranging from fine particle magnets [Pike 1999] to spin transition materials [Tanasa 2005], including the determination of interactions in multiphase magnetic systems [Béron 2008].

In the field of magnetocaloric materials, Basso [2005] implemented a Preisach model to describe the magnetic hysteresis of FOPT materials and extract the adiabatic temperature changes of the sample. This model was extended to describe the temperature dependence of the magnetic hysteresis loops [Basso 2008]. More recently, modifications of this Preisach model have been used to describe the temperature dependence of the phase transformation [von Moos 2014, von Moos 2015]. This model assumes that the Preisach distribution is independent of the intensive variables (field H and temperature T) and produces a qualitative agreement between experiment and model. However, detailed FORC distributions would be needed in order to be able to improve the predictive power of these models.

To date, the application of FORC analysis to magnetocaloric materials has been limited to the study of the interaction field between the phases in a magnetocaloric composite with a SOPT [Franco 2015]. The comparison between the interaction field obtained from the analysis of the magnetocaloric effect [Romero-Muniz 2013] and the results of the FORC analysis shows good qualitative agreement, supporting the presence of these interactions, but giving very different quantitative values. This was explained by the different sensitivity of both techniques, with the MCE being more sensitive to larger interaction fields and the FORC being sensitive to the fields within the irreversibility region.

A well-known family of magnetocaloric materials with a FOPT is the Heusler-type alloys [Hu 2001]. The martensitic–austenitic transition temperature can be shifted by different excitation parameters; we report the effect of varying the applied magnetic field. They exhibit an inverse magnetocaloric effect when the sample transforms from the non-magnetic martensitic phase to the magnetic austenitic phase at higher temperatures.

In this work, we study the temperature and field dependence of the FORC distributions of a Heusler alloy with composition $Ni_{45.7}Mn_{36.6}In_{13.5}Co_{4.2}$ [Gottschall 2015]. It is worth mentioning that this is not the first time that thermal hysteresis is analyzed using FORC, as the temperature hysteresis of spin transition materials was studied before [Tanasa 2005]. What is novel in this letter is its application to magnetocaloric materials. We analyze the influence of the measuring protocol on the FORC distribution, as well as to what extent the assumption of H and T independence made in previously mentioned Preisach models is appropriate for this kind of samples.

II. EXPERIMENTAL

The sample was prepared by arc melting. In order to ensure homogeneity, the melting procedure was repeated several times. Subsequently, the as-cast material was annealed in a quartz tube under 50 kPa Argon atmosphere at a temperature of 1173 K for 24 h followed by water quenching. The final chemical composition was determined by inductively coupled plasma optical emission spectrometry (ICP-OES) confirming a composition of $Ni_{45.7}Mn_{36.6}In_{13.5}Co_{4.2}$, with a resolution better than 1 atomic percent.

The temperature and field-dependent magnetization curves were measured in a vibrating sample magnetometer using a maximum applied field of 5 T. The first-order reversal curves of magnetization versus temperature upon cooling were recorded for applied fields of 1, 2, and 5 T. For the 2 T case, the FORCs were also recorded upon heating. Before each of the temperature sweeps, the magnetic and thermal hysteresis of the sample was erased by completely transforming the sample by cooling down to a temperature well below the transition in zero applied field from a starting temperature well above the transition (the temperature values are given below). This allows us to obtain a repetitive state of the sample for each FORC curve and avoid spurious effects when the magnetization curves are used for calculating the MCE [Kaeswurm 2016, Tocado 2009]. In total, 24 FORC curves were recorded per applied field value, with smaller temperature steps between the reversal temperatures (T_r) in the regions where the larger magnetization changes were taking place. Each curve was measured with experimental points at each 0.5 K.

The FORC distribution was calculated as the crossed derivative of M with respect to T and T_r. The time consuming process of resetting the memory of the sample between each curve and the relatively slow temperature sweep prevented the acquisition of a larger number of FORCs, unlike for $M(H)$ FORC analysis. In order to apply any smoothing algorithm the different resolution in applied temperature T (0.5 K) and the reversal temperatures T_r (with a total of 24 points for each case) has to be considered. While smoothing in T would not reduce the physically meaningful information to a large extent, the limited number of points in T_r forces us to be much more conservative. The option adopted was a modification of Pike's algorithm [Pike 1999], fitting the experimental dataset to a polynomial surface which is linear in T_r and quadratic in T, using a matrix of 3 data points along the T_r axis and 5 along the T axis. This procedure provides a reasonable balance between smoothing and the significance of the distributions.

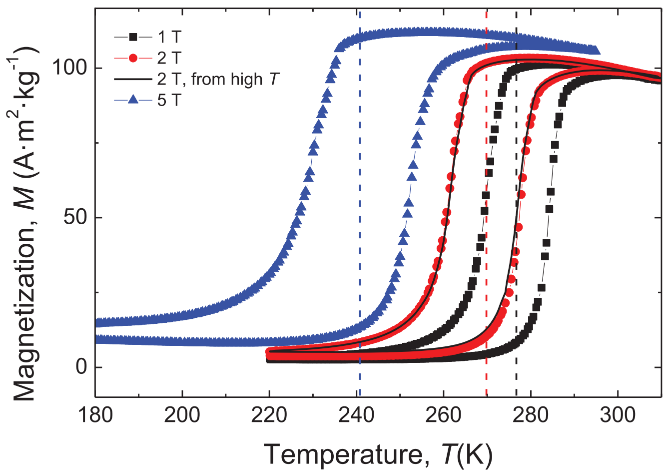

Fig. 1. Magnetization vs. temperature of $Ni_{45.7}Mn_{36.6}In_{13.5}Co_{4.2}$ for different maximum applied fields. The vertical dashed lines indicate the center of the loops. All are measured starting from low temperature saturation, except for the 2 T case, which was measured starting from both low and high T saturation.

III. RESULTS AND DISCUSSION

Fig. 1 shows the $M(T)$ hysteresis loops of the studied samples for applied fields of 1, 2, and 5 T. The transition temperatures of the martensitic–austenitic transformation upon heating and cooling decrease with increasing magnetic field, as well as the widths of the hysteresis loops, in agreement with previously published results [Gottschall 2015]. All loops were measured starting from low temperature saturation, except for the 2 T case, which was also measured starting from the high-T saturation. It can be seen that there is no significant difference between these two saturation loops, indicating that the transformation has been completed in both cases.

Taking into account the asymmetry of the loops, two different protocols can be used for recording the FORC curves. Either a) the transformation can be saturated at high T (310 K for 1 and 2 T applied field; 295 K for 5 T), the temperature is subsequently decreased down to T_r and then the FORC curve is measured with increasing T, or b) the transformation is saturated at low T (220 K for 1 and 2 T applied field; 180 K for 5 T), the sample is heated up to T_r and the FORC curve is recorded during cooling. Figs. 2 and 3 compare these two procedures for an applied field of 2 T, evidencing some qualitative differences in the curves (which will be more evident when analyzing the FORC distributions).

The FORC distributions of the curves presented in Figs. 2 and 3, as well as the FORC curves measured at 1 and 5 T with decreasing temperature are plotted in Fig. 4. In order to determine the origin of the distribution and to generate the T_h and T_u axis, in analogy to the coercivity (H_c) and interaction (H_u) fields usually used in the FORC distributions of $M(H)$ loops, the centers of each of the hysteresis loops were calculated as the center temperature between the peaks of the first derivatives of magnetization vs. temperature (dashed lines in Fig. 1). These values are $T_{center} = 276.7$, 269.8 and 240.8 K for applied fields of 1, 2, and 5 T, respectively, and depend linearly on temperature with a slope of -9 K/T. This linear displacement of the center of the distribution is analogous to the one previously considered for taking into account the effect of magnetic field on the

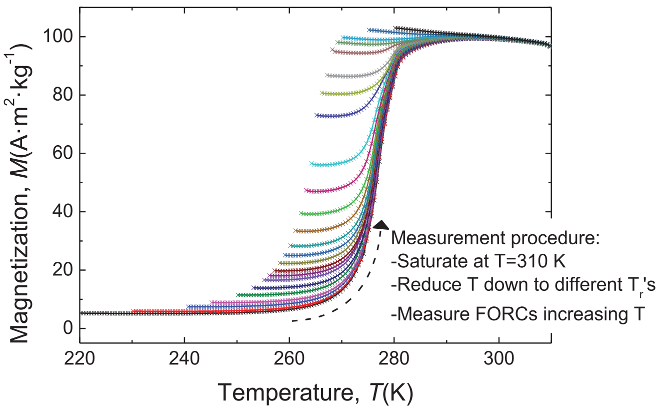

Fig. 2. FORC curves of the loop measured for a maximum field of 2 T. These curves were measured with increasing temperature.

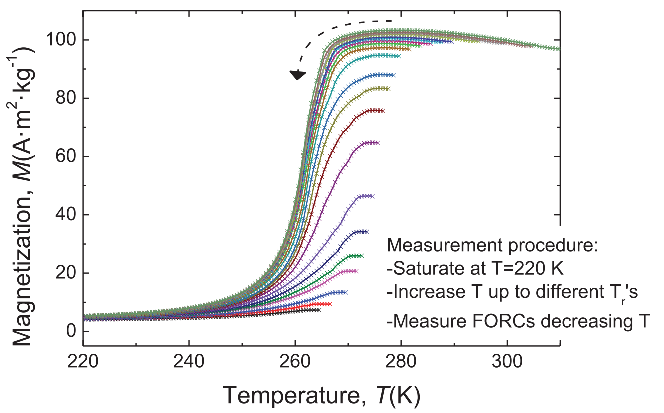

Fig. 3. FORC curves of the loop measured for a maximum field of 2 T. These curves were measured with decreasing temperature.

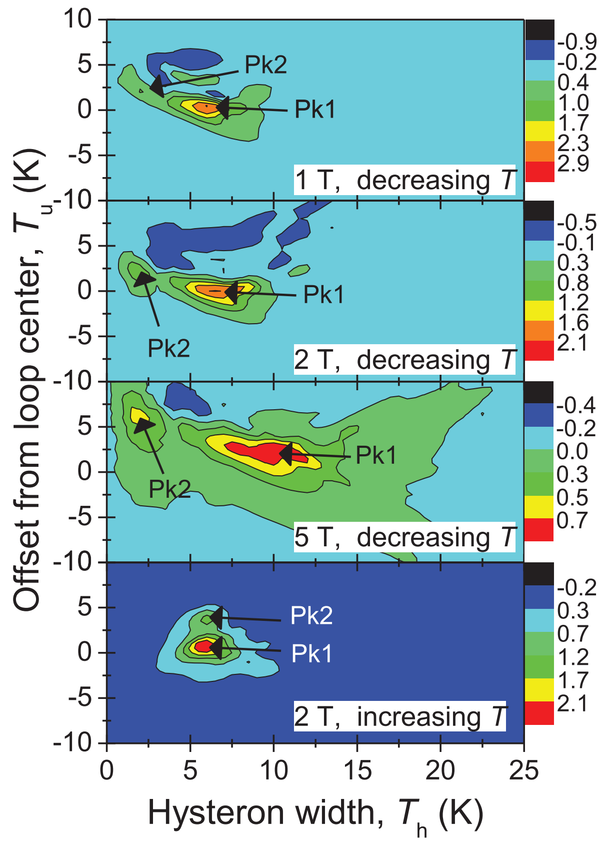

Fig. 4. FORC distribution corresponding to the different measurement conditions. The origin of the distribution is determined from the centers of the loops, as shown in Fig. 1. The major (Pk1) and minor (Pk2) peaks of each distribution are marked by arrows. Note that the T_u axis is referred to the center of the transition, with absolute temperature ranges of 266.7–286.7 K at 1 T, 259.8–279.8 K at 2 T, and 230.8–250.8 K at 5 T.

hysteresis loops [Liu 2012]. Therefore, for an hysteron with transition temperatures T_1 and T_2 and a major loop with center T_{center}, $T_h = (T_2 - T_1)/2$ and $T_u = (T_1 + T_2)/2 - T_{\text{center}}$.

In all cases, two main maxima can be observed in the FORC distribution. The most prominent one lies close to the T_h axis, accompanied by a smaller one shifted along the T_u direction. In the case of the distributions measured with decreasing temperature, the smaller maximum is also shifted to lower T_h values, remaining at the same T_h value of the main maximum for the increasing temperature case. These differences between heating and cooling distributions can be due to the different microscopic details of the martensitic to austenitic and austenitic to martensitic transitions, which are also strongly affected by the different nucleation sites of the different variants. These microscopic details cannot be independently identified by a macroscopic technique like FORC analysis of magnetization curves. However, in order to be able to ascribe these differences to different microscopic processes, further extensive measurements which correlate magnetization to microstructure using dynamic experiments will have to be performed, which is beyond the scope of this letter.

Focusing our attention on the field dependence of the FORC distributions measured with decreasing temperature, even if the qualitative features of the distribution are maintained, there are two main characteristics which are strongly affected by field. On the one hand, the position of the main peak of the distribution shifts along the T_h axis from 6 K for 1 T to 10.5 K at 5 T. This shift is one order of magnitude smaller than the shifts of the centers of the loops along the T axis. Apparently, the main maximum also shifts along the T_u axis with increasing field, although the small magnitude of the shift prevents us from making any further claim because the smoothing algorithm could be playing a role in this latter case. On the other hand, the spread of the distribution over the $T_h - T_u$ plane is larger for larger applied fields, having the side effect of decreasing the maximum value of the FORC distribution peak. Further studies, involving both models and experiments, are needed to give a reliable interpretation of the T_h and T_u axes and to correlate the different features of the distributions to the kinetic parameters of the transition. Nevertheless, it is shown that the field dependent distributions have similar features which can be compared by appropriately shifting the temperature axis, provided that the experimental protocol is kept the same for the comparison.

From the presented distributions it is evident that H and T excitations are actually not independent, as evidenced by two main facts: (i) the shift of the temperature hysteresis loop towards lower temperatures when magnetic field is increased and (ii) the modification of the FORC distributions, making them extend over a broader T_u and T_h regions. The first fact was already well known from magnetocaloric studies, while the alteration of the distribution of hysterons could only be observed after performing this FORC analysis. The link between these two intensive magnitudes (T and H) and how to incorporate simultaneous T and H excitations in Preisach modeling of magnetocaloric materials is a topic which deserves further attention and requires extensive and time consuming experimental measurements, leaving it beyond the scope of this letter.

IV. CONCLUSIONS

The field dependence of the thermal hysteresis loops of a $Ni_{45.7}Mn_{36.6}In_{13.5}Co_{4.2}$ Heusler alloy with promising magnetocaloric properties has been studied using thermomagnetization first-order reversal curves. It has been shown that, even if FORC distributions remain qualitatively the same for different applied fields, quantitative details such as the center of the distribution, its broadening in the $T_u - T_h$ plane and the positions of the maxima are influenced by field, in contrast to the usually assumed independence of the Preisach distributions on the magnitudes of H and T. Consequently, it is necessary to characterize the distributions for different H and T values in order to be able to accurately model the transition.

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