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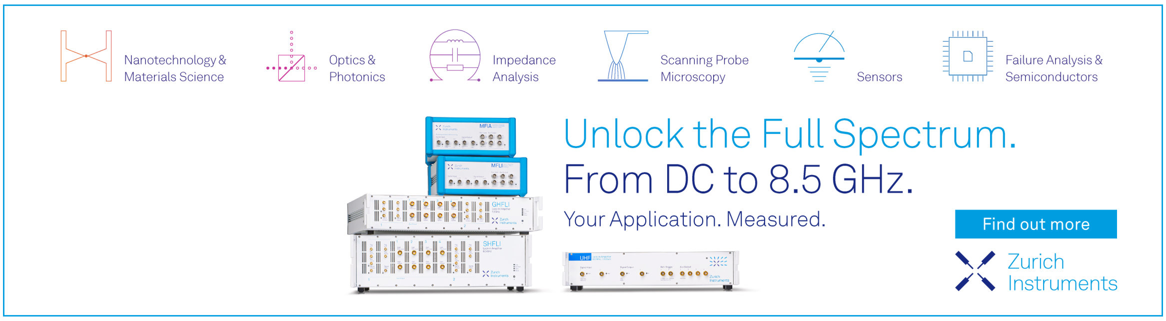

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ABSTRACT

Ferromagnetic shape memory alloys attracted increasing interest as multicaloric materials for solid state refrigeration. The most effective field coupling is achieved through the combination of the magnetic and mechanical induction of thermoelastic martensitic transformation. In the present work, we present an experimental investigation on NiMnGaCu polycrystalline cast alloy, by means of an experimental setup for compression tests in isothermal conditions under a longitudinal magnetic field. The setup has been *ad hoc* designed and developed specifically for this purpose. In this way, we can measure the elastocaloric and magnetocaloric effect at the same time. Moreover, the evolution of the entropy changes ΔS and the functional caloric parameters vs the magnetic field is evaluated. The application of magnetic field seems to act like a supplementary mechanical longitudinal stress. These preliminary results are fundamental to achieve a comprehensive understanding and modeling of coupled multicaloric phenomena.

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Ferromagnetic shape memory alloys (FeSMAs) are promising materials for the exploitation of the caloric effect induced by different kind of fields, e.g., magnetic, mechanical, and electric.[1] The possibility to induce their peculiar thermoelastic martensitic transformation (TMT) upon the field application opens the route to a considerable increase in the entropy change involved in the transformation in order to produce a giant caloric effect. In literature, there are different studies related to the elastocaloric effect[2–4] and to possible coupling with magnetic field in FeSMA.[5–8] NiMnGaCu is one of the most interesting FeSMA, which was studied in the last few years as promising polycrystalline magnetocaloric material.[9–12] The results obtained upon application of high magnetic fields (over 5 T) suggest considering this alloy as reference system for multicaloric approach. The combination with the mechanical effect and, therefore, with elastocaloric properties is a first step of interest. In previous studies,[13,14] we optimized the elastocaloric properties of this alloy, in correlation to the improvement of microstructure, to overcome the intrinsic general brittleness of these materials. In parallel, other investigations were carried out on magnetocaloric properties and on magneto-mechanical coupling, by means of strain recovery tests vs temperature under fixed stresses and magnetic field in an adiabatic calorimeter.[15] Our investigation could be considered a complete stress–strain pseudoelastic test under magnetic field to highlight the effect of simultaneous use of these two driving forces for multicaloric purposes. A few similar investigations are present in the literature about the study of coupling of mechanical and magnetic fields.[16,17] In Ref. 16, we have an interesting comparison on the effect of magnetic field on critical stress for the reorientation of martensite and stress induction of martensite, and in our work, we present the experimental coupling that in Ref. 17 is presented only using Landau theoretical numerical approach. The results obtained in our previous work demonstrated that with suitable thermal treatment, the efficiency of TMT could be tuned in this alloy, and we are able to introduce in the polycrystalline samples a grain microstructure with improved mechanical properties. This allows us to have good repeatability of the mechanical curves despite the inevitable intrinsic fragility of this alloy.[13,14] Then, we obtained sufficient mechanical stability to organize

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elastocaloric investigation and to design its coupling with the magnetic field.

The set up prepared is shown in Fig. 1: we employed two ring-shaped permanent magnets (stable up to 250 °C) inserted in the cylindrical box, which produce longitudinal magnetic field of 0.1 and 0.5 T in the hollow part. The value of the magnetic field produced was tested by Hall probe, and the values indicated are a medium data along the length of about 10 mm. The measures were performed in the E3000 Instron mechanical test instrument with a load cell of 3 KN in a thermal chamber for precise control of the isothermal conditions. The magnetic setup was mounted around cylindrical quartz compression platens of 10 mm of diameter and 50 mm of length. During the first step of the measure to reach the established condition of measurements, the sample was hold in the setup by a low stress of 3 MPa applied in compression configuration. The thermal chamber was programmed in heating control to the temperature of the test, with the temperature ramp of 5 °C/min and maintained for 30′ at the final temperature, to assess and reset all the thermal expansion of the system. The control of the temperature around the sample is performed by a thermocouple near the sample. After the control of reaching of the test temperature, the mechanical measurements were conducted in compression configuration, in isothermal conditions in the temperature range 343–363 K. To avoid the break of these brittle samples, we control the measure in stress, and we performed the test in stress control with a rate of 20 MPa/min. The stress was determined by the load cell signal and the accurate direct measure of the sample section. By optical extensometer associated with the machine, we measured the strain of the sample, and we set the final stress to have up to 4% of strain. The accuracy of optical extensometer coupled with the system is periodically controlled, and the systems transfer the deformation without internal loss of movement.

The prepared and investigated samples are polycrystalline ferromagnetic $Ni_{50}Mn_{18.5}Ga_{25}Cu_{6.5}$(at%) obtained by arc melting, cut in rectangular shape of size 3 × 3 × 8 mm, and heat treated at 1123 K for 6 h under vacuum conditions to have sufficient mechanical repeatable performances. In Fig. 2, we show together with the first example of magnetic field effect on mechanical stress–strain curve, the DSC control for three consequent thermal cycles of the tested sample, which shows stable TMT with Ms = 322.4 K and Af = 333.6 K. In the graph,

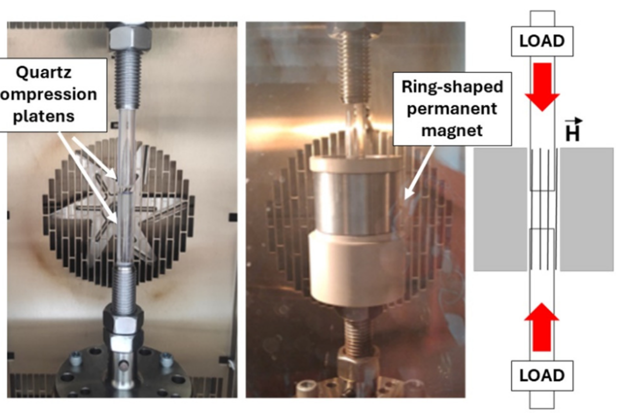

FIG. 1. Picture and scheme of the experimental setup for the application of longitudinal magnetic field between quartz compression platens.

we highlight the overlying of this transition with change in Heat Capacity at Curie Temperature, giving the principal condition for overlapping of thermodynamic second order magnetic transition and first order TMT transition. In this case, this overlapping opened interesting perspectives for magnetocaloric effect,[10] where the application of magnetic field induces all the two transitions with consequent giant Entropy Change. However, the single magnetocaloric effect requests very high magnetic field (also 9 T).[10] In our study, we consider the application of mechanical stress longitudinal field coupled with magnetic field. We induce martensitic transition by stress, and we investigate the effect of inducing at the same time magnetic order in ferromagnetic martensite. The compression measure is carried out starting from 343 K, which corresponds to material in austenite paramagnetic state at Af + 10 K; the other testing temperatures were chosen ranging in the interval of 343–363 K; therefore, we consider in any case the starting material in paramagnetic austenite phase. Each curve was registered upon heating to next temperature. Due to the absence of residual strain, it is not necessary to go to higher temperature to completely transfer the material in austenite phase.

In Fig. 2, we report the comparison between the stress–strain curves registered at 343 K at two different fixed applied magnetic fields. By observing the graphs, it is possible to describe the results obtained as follows: in Fig. 2, we report the first comparison among the curves registered at 343 K without and under magnetic field. At 343 K, the sample is in austenitic paramagnetic phase, and by applying the stress, we register the typical curve for Shape Memory Alloys with the induction of detwinned martensite in loading step and recovery of austenite phase by shrinking of martensite in unloading step, due to removal of the stress. Mechanical hysteresis is associated with this process. When we apply stress and at the same time the magnetic field, the mechanical curve changes significantly because the induced martensite is detwinned in the stress direction but also magnetically ordered, with the alignment of the dipoles along longitudinal magnetic field applied. This effect is more evident with increasing of the magnetic field, and we observe generally decreasing of critical stress to induce martensite and the lowering of evidence of critical stress. Then, more evidence of linear behavior appears, and an increase in total strain reached at the same final stress applied happens. Moreover, we can resume and highlight the principal effects of simultaneous application of stress and magnetic field as follows: (1) the increase with H of the maximum strain achieved at fixed stress, (2) the increase in quasi-elastic behavior of the martensite detwinning and the reduction of the visibility of the critical point correspondent to stress induced martensite (SIM) and its detwinning plateau, (3) the reduction of the critical stress for the martensite induction upon H increasing, and (4) the reduction of the mechanical hysteresis.

Starting from this first observation, we registered the mechanical curves at different temperatures and under two fixed magnetic fields H. In Fig. 3, we show a selection of the most interesting curves for the three values of magnetic field.

We elaborated these curves by discrete integration at different strain values following the Maxwell relationship described in Eq. (1), to obtain a first description of the trend of entropy change vs test temperature.[18] The results are reported in Fig. 4 for loading and unloading stages,

$$\Delta S = -\int_0^{\varepsilon} \frac{\partial \sigma}{\partial T}\, d\varepsilon. \tag{1}$$

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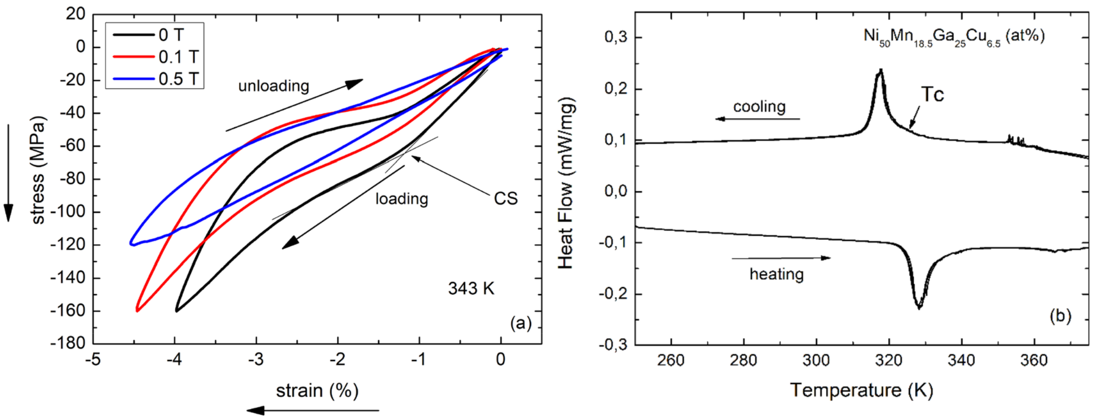

FIG. 2. (a) Compressive stress–strain curves registered at 343 K for three values of magnetic field H: 0, 0.1, and 0.5 T and (b) calorimetric analysis on three thermal cycles. The CS point indicates the critical stress of martensite induction.

The Clausius Clapeyron (CC) coefficient is defined as $\boldsymbol{k} = \boldsymbol{d\sigma/dT}$, and it is a basic parameter that describes the linear relationship between critical stress to induce TMT and temperature. The $\boldsymbol{k}$ coefficient is derived as cross point of tangents on the elastic part and plateau, and it corresponds to the critical stress value that the material must reach to induce martensite by stress or the stress value where the curve changes its slope.[19] Some discrepancy in the trend of the data in Fig. 4 (i.e., in correspondence to 0.03 strain at 0 T) is due to non-perfect linear behavior of CC relationship. From the same series of curves, we obtained also the coefficient $\boldsymbol{k}$ vs H. The values obtained for 0 T of the linear regression agree with our previous results for polycrystalline samples,[14] and they are lower than the general value of 5 MPa/K referred to NiMnGa system and derived alloys.[20,21] Moreover the increasing of H field induces a decrease of critical stress and related $\boldsymbol{k}$ CC coefficient.

In Fig. 5, we show a resume of $\boldsymbol{k}$ values, the maximum value registered for entropy change ΔS max and mechanical hysteresis.

Analyzing these series of mechanical curves, we can try to individuate the physical origin of the principal effect induced by magnetic fields. It seems that the H acts as an overlapped longitudinal force applied to the material. This effect decreases the longitudinal mechanical stress required to generate SIM and increases the total strain reached at the same final stress. When we start the compression, we reach the stress level to induce martensite, and the application of the magnetic field induces the deformation of the twins to align the dipoles along the direction of the applied field. This martensite structure is detwinned in an easier way and at lower stress. The random distribution of magnetic twins domains influences also the distribution of this deformation and causes the smoothing of the loading curve to a quite elastic curve, where there is not a precise critical stress to induce and then detwin the martensite. In fact, this structure is more homogeneously distributed in the material, and it is transformed or detwinned in correspondence of a more widespread range of stresses. Moreover, at the beginning of the stress–strain curves obtained at highest magnetic field and higher temperature (Fig. 3), it seems that there is an initial elastic deformation of martensite already oriented along the stress direction by the effect of the magnetic field. Therefore, the increase in critical stress with temperature is consequently reduced, and the shape of the curves is more linear by increasing the magnetic fields. It is not trivial to note that this evident effect in mechanical curves is obtained with low values of magnetic field, at most 0.5 T. This observation is interesting since it evidences the synergy of the two driving forces. Indeed, the mechanical and magnetic fields act collaboratively for potential caloric applications, and we can achieve an interesting effect with stress and magnetic field values significantly reduced with respect to single elastocaloric or magnetocaloric effect.

The values of entropy change calculated reflect the general variability presented in the literature; the results obtained by mechanical approach agree with our previous results.[14] The high value measured at 0 T could be due to induced ordered martensite respect to twinned martensite obtained in only calorimetric approach; moreover, some influence is due to approximation by discrete integration for stress–strain curves and to intrinsic overestimation derived to the use of Maxwell equation in first order transition's case. The evaluation of ΔS is derived only from the mechanical point of view, and we obtain generally a decrease in the values by increasing the magnetic field H. For H = 0 T, we obtain the maximum value of 36 and 66 J/(kgK) for loading and unloading curves, respectively. These values decrease to 11 and 30 J/(kgK) for H = 0.5 T. These results show the same trend with a previous investigation,[15] where the magnetic field is applied in strain recovery under fixed stress measures. However, we must highlight some important differences. First of all, the value of magnetic field in ref is significantly higher (up to 6 T).[15] Second, we observe, with a little increase in the magnetic field (from 0 to 0.5 T), a total reduction of the entropy change value of almost 50%, while the lowering expressed in strain recovery curves is above 11% at different applied stresses. However, this discussion is still very open, due to the absence of similar experimental results in the literature, and a complete numerical interpretation is necessary to well understand the caloric physical phenomena in this kind of experimental investigation by direct stress–strain measures. A further consideration becomes necessary: in Ref. 15, the contribution of the magnetic field is calculated using an adiabatic calorimeter. In this case, we have the application of magnetic field during strain recovery test at low stress (max 20 MPa). The induction of TMT and then the caloric effect is induced by two driving forces at the same time: magnetic field and temperature change, and the stress applied acts in the detwinning of martensite. All the caloric effects are

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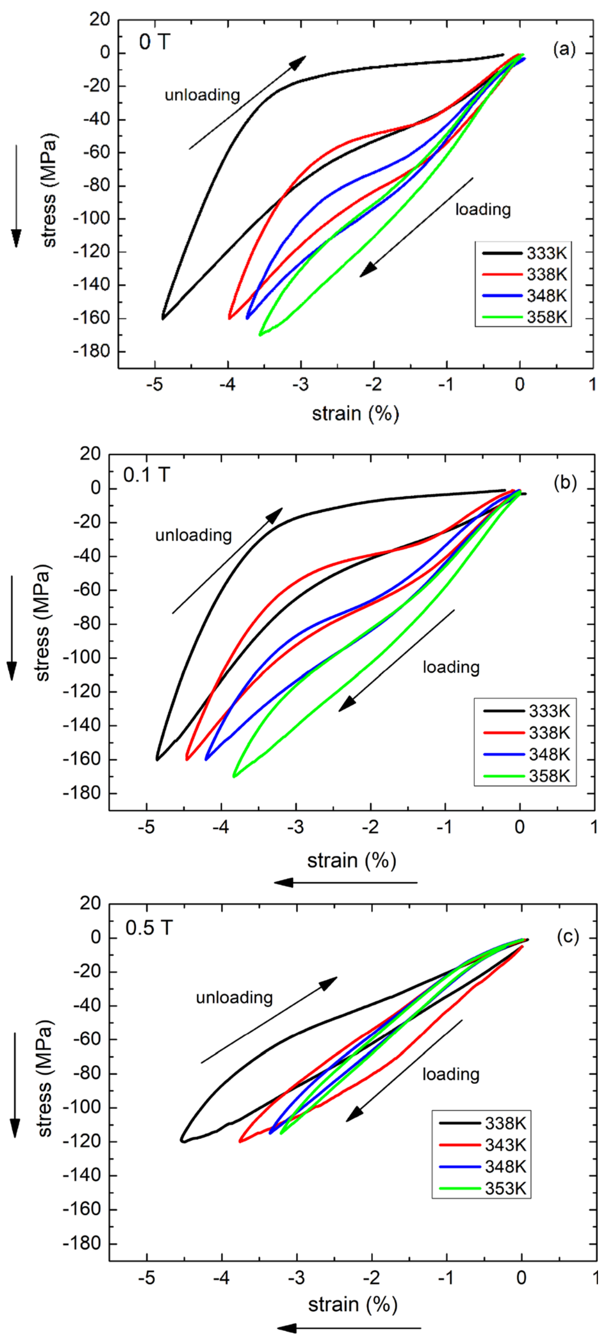

FIG. 3. Compressive stress–strain curves registered at different temperatures and under different magnetic fields: 0 T for (a), 0.1 T for (b), and 0.5 T for (c).

measured because the experimental data considered are the Enthalpy registered by the calorimeter. By analyzing this parameter, it is possible to obtain the total entropy change and also the ΔT evaluation. In our work, a further reflection is necessary to better understand the completeness of the evaluation of changes in entropy. It is possible that, in this way, we consider only the contribution of elastocaloric effect, and to evaluate the complete multicaloric effect, we must measure the adiabatic ΔT values. In fact, we analyze the change of mechanical curve, and from these experimental data, we obtain the entropy change.

Finally, the graph that resumes the values of entropy change confirms, for elastocaloric effect, a better efficiency in entropy change correspondent to unloading step. It seems that the application of magnetic force favors this discrepancy with the loading correspondent value. This aspect agreed with the previous observation in the magnetocaloric effect[10,13] and in investigation using strain recovery test.[14,15]

The effect of magnetic field is the change in the critical stress, in the slope and in the hysteresis of mechanical curve; therefore, it must be investigated in deep if the thermal effect of the magnetic order is enclosed in these changes or if it could be measured only by ΔT measures and by the compression test, we have feedback on improving only elastocaloric effect by the magnetic field. Finally, this kind of measure considers the induction of martensite principally by stress, which is a way that could not be able to transform all the material and could cause localized plastic deformation. It is possible to underestimate the TMT transition and its caloric effect correlated. Now, the measure of ΔT under magnetic field, by thermocouples system, is not completely assessed with sufficient reliability, but the development of this aspect is in progress to complete and to give this important information about our investigation. However, these results obtained by stress–strain curves give important information about the increase in the caloric efficiency obtained using high stress and low magnetic field, with respect to the application of high magnetic field and low stress. Therefore, this route appears to be the more efficient in terms of application perspectives. Another preliminary interesting indication (Fig. 4) is that with the increase in the magnetic field, also the maximum value of entropy change is shifted toward higher temperatures; so, it seems that it is possible to tune the temperature window for multicaloric effect by applying magnetic fields.

The values obtained for the ***k*** Clausius Clapeyron coefficient confirm the effect of magnetic field as a supplementary oriented force applied to the material, which reduces the increasing of the stress with the temperature and, consequently, reduces ***k***. Finally, a mention is due to the trend of the mechanical hysteresis vs magnetic field. The deformation of martensite induced by magnetic field also reduces the difference in the stress level correspondent to the loading and unloading steps of the curves. The energy difference between the direct and inverse transformations is narrower because the energy loss during the induction and shrinking of martensite is reduced. In fact, the detwinning of martensite is more favorable starting from magnetically ordered martensite, and its shrinking starts from a higher level of unloading stress. This could be a positive effect on the coefficient of performance of the elastocaloric effect, on cycling stability and general fatigue resistance of the material.

A further comparison could be executed with similar experimental results obtained on NiMnGaIn and NiMnCuGaSn.[20,22] Even if the magnetic field used is higher (up to 4 T), also in these works, the effect of application of magnetic field with multicaloric purposes is to reduce the critical stress and the mechanical hysteresis and to increase the maximum strain reached.

This series of magneto-mechanical coupled experiments shows the principal effects of the application of magnetic field in compressive stress–strain curves for multicaloric perspectives. This combination of mechanical and magnetic driving forces contributes to the reduction

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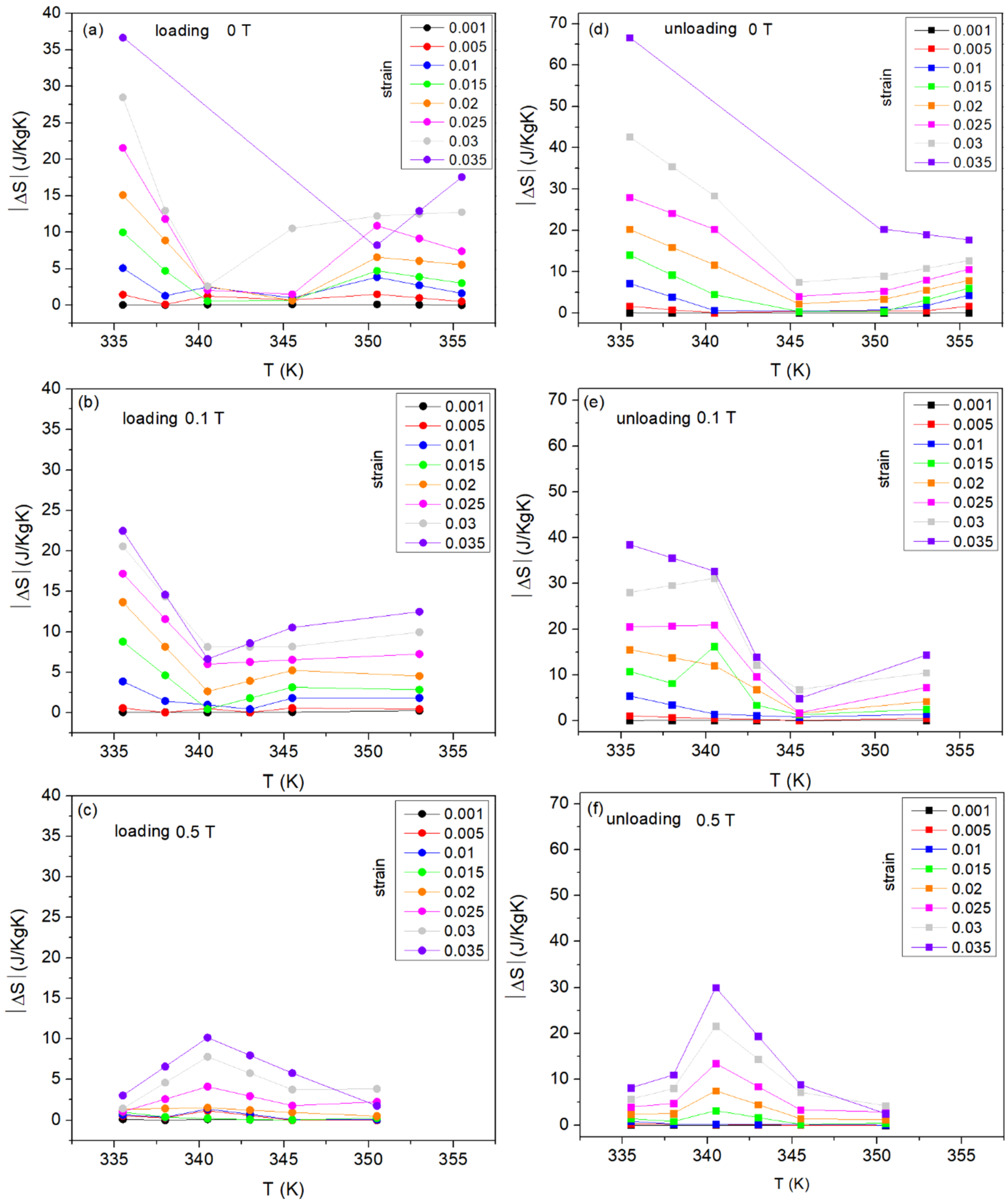

FIG. 4. Calculated entropy change (ΔS) values vs Temperature for loading [(a)–(c)] and unloading stages [(d)–(f)], under 0, 0.1, and 0.5 T magnetic fields at different strains. For graphs at 0 T (a) and (d), the lack of data correspondent to 0.035 in strain is due to difficult in experimental conditions.

of the value of magnetic field to obtain magnetocaloric effect and to increase the efficiency of the coupling with the elastocaloric effect. In our investigation, we apply, at the same time, stress and magnetic field; the first induces the TMT, and the second induces the magnetic order; the two forces help each other to bring about the two transformations. Therefore, we could consider the first as the elastocaloric effect and the second as the magnetocaloric effect, and we have, in this kind of curve, the multicaloric effect due to the combination of two driving forces. In this kind of investigation, we measure the elastocaloric and magnetocaloric effects at the same time. In this case, the magnetic order is introduced with low magnetic field in comparison with the pure magnetocaloric effect. Particularly, the principal parameters that are

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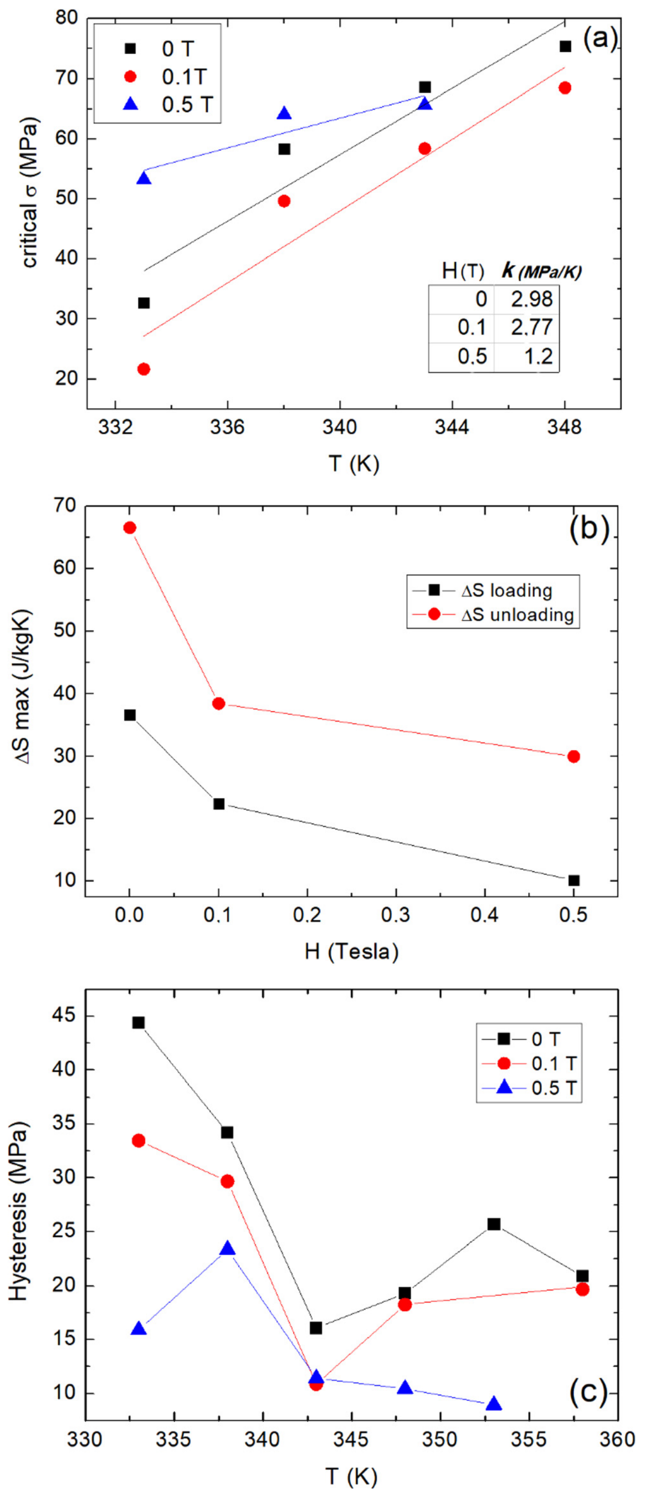

FIG. 5. (a) Critical stress for SIM vs Temperature, and the inset shows the value for CC coefficient ***k***, (b) ΔS maximum peak vs H applied magnetic field, and (c) mechanical hysteresis values at medium strain vs temperature and at different H applied magnetic fields.

involved and optimized in these measurements are the critical stress, the total strain, and the reduction of loss of mechanical energy in the hysteretic process.

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

F. Villa: Data curation (equal); Investigation (equal); Writing – original draft (equal). **E. Bassani:** Investigation (equal). **F. Passaretti:** Methodology (equal); Writing – review & editing (equal). **C. Tomasi:** Methodology (equal); Writing – review & editing (equal). **E. Villa:** Conceptualization (lead); Data curation (lead); Investigation (equal); Writing – original draft (equal).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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