Magnetic and structural entropy contributions to the multicaloric effects in Ni-Mn-Ga-Cu

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We have studied the multicaloric properties of a Ni-Mn-Ga-Cu alloy. In this alloy, application of magnetic field and uniaxial stress shift its martensitic transition towards higher temperatures which results in synergic magnetocaloric and elastocaloric effects. By a proper numerical treatment of the calorimetric curves obtained under applied magnetic field and uniaxial stress we have obtained the entropy change of \( \Delta S \) as a function of the magnetic field, uniaxial stress, and temperature over the whole phase space under study. We have determined the different entropy contributions to the multicaloric effect in this alloy, and noticeably we have evidenced the role played by the interplay between magnetic and vibrational degrees of freedom. A comparison between single caloric and multicaloric effects shows that appropriate combinations of magnetic field and stress reduce the magnitude of the specific field required to obtain a given value of the isothermal entropy and adiabatic temperature changes. For example, at 299 K, to achieve an entropy change \( \Delta S \) of \(-14 \text{ J kg}^{-1} \text{ K}^{-1}\), a magnetic field of \( \sim 2.5 \text{ T} \) or a uniaxial stress of 19 MPa are required, while a combination of dual fields of (1 T, 12 MPa) yields to the same value of \( \Delta S \). Moreover, the maximum adiabatic temperature change is enlarged up to 9.4 K by the dual fields, higher than the value obtained by a single field (\( \sim 7 \text{ K} \)). The advantage of multicaloric effect is particularly relevant at low magnetic fields which are achievable by permanent magnets. Our findings open new avenues for using multicaloric materials in novel refrigeration technologies.

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I. INTRODUCTION

Solid state refrigeration relying on calorific effects in solids is acknowledged as the most promising technology to replace the current vapor compression based refrigeration thanks to its high efficiency and extremely low greenhouse effect potential value [1]. Caloric effects are quantified by isothermal entropy (\( \Delta S \)) and adiabatic temperature (\( \Delta T \)) changes, which are induced by application and removal of external field(s) including magnetic field [2] (magnetocaloric effect), electric field [3] (electrocaloric effect), uniaxial stress [4,5] (elastocaloric effect), and hydrostatic pressure [6] (barocaloric effect).

Materials with large calorific effects, associated with a first-order phase transition, have been discovered in the past two decades [7–11], and the recent emergence of a series of materials with colossal calorific effects has further fueled the research on this topic. Among them, colossal barocaloric effect in plastic crystals with isothermal entropy changes in the range 300–500 J kg\(^{-1}\) K\(^{-1}\) have been reported [12–14]. Another family of promising calorific materials are spin-crossover complexes, in which huge [15] and reversible [16] barocaloric effects were achieved. In addition to these barocaloric materials, encouraging elastocaloric materials have also been discovered, such as all-\(d\)-metal Heusler alloys [17,18]. This kind of new alloys show improved mechanical properties (breaking strength \( > 1.2 \) GPa) [19] and large latent heat (up to 76 J kg\(^{-1}\) K\(^{-1}\)) conferring them a significant barocaloric effect [20,21] and an outstanding elastocaloric effect [22–24].

While improving the absolute value of \( \Delta S \) and \( \Delta T \) [7] is a requisite for potential use of the materials in applications, there are also other parameters which also play a relevant role because they determine the energy efficiency and cyclability of a calorific material [25–27]. These are hysteresis effects and a lower field to induce the phase transition (critical field). Various strategies including tailoring lattice compatibility between parent phase and product phase [28], texture...
control [29], second-phase introduction [30], and additive manufacturing [31] were adopted to reduce hysteresis and to lower the critical field. For those materials with coupling between different degrees of freedom, application of more than one type of external field provides a strategy for controlling hysteresis [32] and/or lowering the critical fields [33].

The simultaneous or sequential change of more than one external field gives rise to the so-called multicaloric effects [34]. The thermodynamic framework of multicaloric effects is well established [35], but its experimental study is just at the beginning [36–39]. Materials that can be triggered by either a magnetic field or a mechanical field, or combination of the two fields, are the focus of interest in multicaloric effect research [40]. It was reported that, for Fe-Rh, applying pressure and magnetic field properly enables control of the sign of the entropy change, and expands the temperature window for multicaloric [37] effects. Recently, it was shown that in Ni-Mn-In the multicaloric isothermal entropy change resulting from the combined action of a 1 T magnetic field and a 40 MPa uniaxial stress was significantly larger than the value resulting from a single stimulus [33]. Furthermore, a hydrostatic pressure of ~1 GPa was found to be able to enhance the magnetocaloric effect by 8% in Ni-Mn-In alloys [41].

The study of multicaloric effects has mainly been conducted on materials with inverse magnetocaloric effect and conventional mechanocaloric effects. In these materials, the magnetoestructural phase transition takes place from a ferromagnetic high temperature phase to a low magnetization martensite [47]. Thermomagnetization curves (Fig. S1 in the Supplemental Material [47]) at selected values of magnetic field confirm the overlapping of martensite and magnetic transitions. The alloy undergoes a transition from a paramagnetic austenite to a ferromagnetic martensite.

In the prototype Ni$_2$MnGa magnetic shape memory alloy, it is known that substitution of Mn with Cu shifts the martensitic transition (MT) to higher temperatures while it decreases the Curie temperature [45]. The two transition lines joint at a triple point close to 6 at % Cu. As a result, the strength of the interplay between the structural and magnetic transitions increases as the amount of Cu increases and a magnetoestructural transition from a paramagnetic high temperature parent phase to a ferromagnetic martensitic phase which gives rise to synergic calorific effects.

In the prototype Ni$_2$MnGa magnetic shape memory alloy, it is known that substitution of Mn with Cu shifts the martensitic transition (MT) to higher temperatures while it decreases the Curie temperature [45]. The two transition lines joint at a triple point close to 6 at % Cu. As a result, the strength of the interplay between the structural and magnetic transitions increases as the amount of Cu increases and a magnetoestructural transition from a paramagnetic high temperature parent phase to a ferromagnetic martensitic phase takes place above 6 at % Cu. Therefore, this material is expected to be a good candidate to show synergic magnetocaloric and elastocaloric effects. With this idea in mind, in the present work we have prepared a Ni$_{50}$Mn$_{18.5}$Ga$_{25}$Cu$_{6.5}$ alloy to study its multicaloric response under the combined application of uniaxial stress and magnetic field. A bespoke calorimeter that works under magnetic field and uniaxial stress has been employed to determine entropy changes as a function of temperature, magnetic field, and uniaxial stress.

Based on these results, multicaloric as well as single calorific effects for the synergic-type Ni$_{50}$Mn$_{18.5}$Ga$_{25}$Cu$_{6.5}$ have been systematically investigated.

II. EXPERIMENT

An ingot with nominal composition Ni$_{50}$Mn$_{18.5}$Ga$_{25}$Cu$_{6.5}$ was prepared by arc-melting high-purity metals and then suction casted into a rodlike sample with a diameter of 7 mm in a copper mold. A crystallographically oriented polycrystalline rod was grown using the suction casted rod by the liquid-metal-cooling directional solidification method with a pulling rate of 150 μm s$^{-1}$. Specimens with 3 mm diameter and 6 mm length were cut from the rod and were annealed at 1073 K for 24 h in an Ar atmosphere followed by quenching into a mixture of ice and water.

Calorimetric curves were measured using a bespoke calorimeter upon heating and cooling in a dual-field condition with applied magnetic fields up to $\mu_0H = 6$ T, and applied uniaxial compressive stresses up to 20 MPa. The system is able to perform dilatometric measurements simultaneously. A detailed description of this system can be found in Ref. [44]. The transition entropy changes in the absence of applied magnetic field and applied uniaxial stress for both heating and cooling were determined from calorimetric curves obtained using a commercial DSC TA-Q2000.

Specific heat measurements of the sample at the martensitic and austenitic phases were performed using two different systems. On the one hand, a Physical Properties measurement system (PPMS, Quantum Design Inc.), operating in the relaxation method, was used to perform measurements within the temperature range from 330 to 400 K, under constant applied magnetic fields from 0 to 6 T (in 1 T steps). On the other hand, a Peltier cell calorimeter, described in detail in Refs. [45,46], was used to perform measurements within a temperature range from 50 to 350 K under constant applied magnetic fields from 0 to 3 T (in 1 T steps).

III. RESULTS AND DISCUSSION

Thermomagnetization curves (Fig. S1 in the Supplemental Material [47]) at selected values of magnetic field confirm the overlapping of martensite and magnetic transitions. The alloy undergoes a transition from a paramagnetic austenite to a ferromagnetic martensite.

Figures 1(a)–1(d) show the baseline corrected calorimetric curves obtained at selected values of magnetic field and under applied stresses of 0 and 20 MPa. The complete set of raw calorimetric curves is given in Fig. S2 (Supplemental Material [47]). Endothermic and exothermal peaks are observed upon heating and cooling, corresponding to the reverse and forward MT, respectively. Uniaxial stress and magnetic field shift the martensitic transition to higher temperatures due to the increase in stability of the ferromagnetic martensitic phase.

The forward and reverse transition temperatures can be identified by the temperature of the peak in the calorimetric curves recorded on cooling and heating, respectively. The magnetic field dependence of MT temperatures at constant values of the applied stress is shown in Fig. 1(e) and the stress dependence of the MT temperatures at constant values of the magnetic field is shown in Fig. 1(f). The complete phase diagram showing the transition temperatures in the $H$-$\sigma$ space is given in Fig. SS(a) of the Supplemental Material [47]. It is

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apparent that, at constant stress, the MT temperatures linearly increase with increasing magnetic field, with slopes in the range 0.9 to 1.6 K T$^{-1}$. Furthermore, the value for the slope in the absence of applied stress ($\frac{dT}{d\mu_0 H} = 1.3 \pm 0.1$ K T$^{-1}$) is in good agreement with the value obtained in a previous study [29]. Application of uniaxial stress has little effect on the slope of the $T$ vs $H$ lines, and no clear tendency has been observed [Fig. 1(g)]. MT temperatures also increase with increasing uniaxial stress, with slope values in the range $\frac{dT}{d\sigma} = 0.26$ to 0.38 K MPa$^{-1}$, with a weak dependence on magnetic field [Fig. 1(b)]. The synergic effect of magnetic field and uniaxial stress observed in Ni$_{50}$Mn$_{18.5}$Ga$_{25}$Cu$_{6.5}$ where both magnetic field and stress shift the MT towards higher temperatures is in contrast to the behavior reported for metamagnetic shape memory alloys, such as Ni-Mn-In [33] and for Fe-Rh [37] in which magnetic field stabilizes the high temperature ferromagnetic phase thus shifting the magnetostructural transition to lower temperatures.

The transition entropy change ($\Delta S_t$) can be obtained from integration of the baseline corrected calorimetric curves (details are given in the Supplemental Material [47]), and results are shown in Fig. 2(a) where $\Delta S_t$ corresponding to forward and reverse MT are plotted as a function of magnetic field for selected values of uniaxial stress (a three-dimensional plot of $\Delta S_t$ vs $H$ and $\sigma$ is given in Fig. S5(b) of the Supplemental Material [47]). For all values of applied uniaxial stress, $\Delta S_t$ has been found to decrease with magnetic field, with slopes in the range $-1.1$ to $-0.7$ J kg$^{-1}$ K$^{-1}$ T$^{-1}$. For Ni$_{50}$Mn$_{18.5}$Ga$_{25}$Cu$_{6.5}$ the vibrational and magnetic contributions to the transition entropy change have the same sign, and the expected increase of the magnetic contribution with increasing magnetic field cannot account for the observed decrease in the transition entropy change (in contrast to what happens in other metamagnetic shape memory alloys for which vibrational and magnetic contributions have a different sign [48]). The magnetic field dependence of $\Delta S_t$ found here may point to a certain interplay between the vibrational entropy and magnetic field. This hypothesis is supported by the enhanced softening at the Curie point of the low energy phonons in the TA$_2$ branch in composition related Ni-Mn-Ga alloys [49]. It is to be noticed that for metamagnetic shape memory alloys the vibrational contribution to the transition entropy change is magnetic field independent to a very good extent [48]. Further studies are required to clarify this issue, which is beyond the scope of the present work.

The combination of DSC calorimetric curves recorded under external applied fields and specific heat ($C$) data enables computation of caloric effects via the quasidirect method [9] (details for this computation are provided in the Supplementary Material [47]). While $C$ can be considered as stress independent, for Ni$_{50}$Mn$_{18.5}$Ga$_{25}$Cu$_{6.5}$, as previously mentioned, phonons are sensitive to the applied magnetic field, and $C$ is expected to be magnetic field dependent too. We have measured $C$ at selected values of magnetic field, and results for $\mu_0 H = 0, 1, 2, 3$ T are shown in Fig. 2(b). It is apparent that application of magnetic field sharpens the calorimetric peak and shifts it to higher temperatures at an approximate rate of 1.4 K T$^{-1}$, which is in good agreement with the shift observed from the DSC measurements [see Fig. 1(e)].

The transition entropy values derived from the integration of these peaks decrease with increasing magnetic field at a rate $\sim -0.5$ J K$^{-1}$ kg$^{-1}$ T$^{-1}$, which is consistent with the data shown in Fig. 2(a). Additional specific heat measurements are given in Fig. S4 (Supplemental Material [47]).

Taking into account the magnetic field and temperature dependence of $C$ and using the baseline corrected DSC calorimetric curves we have computed the entropy curves $S(T, \mu_0 H, \sigma)$, referenced to the the entropy value at $T_0 = 426$ K. The value of $T_0$ has been selected to be the temperature where the specific heat becomes magnetic field independent.
FIG. 2. (a) Magnetic field dependence of the transition entropy change at selected values of uniaxial stress. TA denotes the value at zero magnetic field and zero stress obtained using a commercial TA DSC. Open symbols correspond to the forward transition on cooling and solid symbols, to the reverse transition on heating. Lines are the best fit to the data. (b) Temperature dependence of the ratio between specific heat and temperature as a function of temperature for selected values of magnetic field. The inset shows the magnetic field dependence of the transition entropy change derived from the integration of the curves.

[see the Supplemental Material [47] Fig. S4(c)]. The temperature dependence of $S(T, \mu_0 H, \sigma)$ upon heating and cooling for selected values of magnetic field and uniaxial stress are shown in Fig. 3. In the low temperature region (in the martensitic phase) the increase in entropy with increasing magnetic field reflects the dependency of $\Delta S$ with magnetic field [see Fig. 2(a)].

As described in the Supplemental Material [47], the entropy curves enable computing single caloric (magnetocaloric and elastocaloric) effects. Results are given in the Supplemental Material [47] (Figs. S9– S12). As anticipated by the positive shift of the transition temperatures with uniaxial stress and magnetic field, both elastocaloric and magnetocaloric effects are conventional for Ni$_{50}$Mn$_{18.5}$Ga$_{25}$Cu$_{6.5}$.

Entropy curves $S(T, \mu_0 H, \sigma)$ computed from experimental data are only known for selected values of stress and magnetic field, and to obtain multicaloric effects over the entire $(T, \mu_0 H, \sigma)$ thermodynamic phase space it is necessary to define a numerical function to phenomenologically reproduce the behavior of the experimental isofield entropy curves over the entire phase space under study. Details of the fit are given in the Supplemental Material [47], and the results of the field for specific values of magnetic field and stress are compared in Fig. 3 to the curves directly computed from experimental data (additional curves are shown in Fig. S6, Supplemental Material [47]). A good agreement is observed between the two set of curves. Isofield and isothermal entropy surfaces are computed from the fitted entropy curves and illustrative examples for selected values of magnetic field, uniaxial stress and temperature are shown in Figs. S7 and S8 (Supplemental Material [47]).

The entropy and temperature changes associated with single caloric and multicaloric effects can readily be computed from the fitted $S(T, \mu_0 H, \sigma)$ functions as described in the Supplemental Material [47]. The values obtained for the elastocaloric and magnetocaloric effect (Figs. S13 and S14, Supplemental Material [47]) are in good agreement with those previously derived from the experimental curves. Such an agreement confirms the robustness of our fitting procedure and provides confidence in the multicaloric data derived from the fitted $S(T, \mu_0 H, \sigma)$.

In Ni$_{50}$Mn$_{18.5}$Ga$_{25}$Cu$_{6.5}$, both magnetic field and uniaxial stress favor the transition from austenite to martensite (as cooling does), and therefore the multicaloric effect resulting from application of magnetic field and uniaxial stress has to be computed from the entropy functions corresponding to
cooling runs. On the other hand, the multicaloric effect resulting from the removal of magnetic field and uniaxial stress has to be computed from the entropy functions corresponding to heating runs. Illustrative results for the multicaloric $\Delta S$ and $\Delta T$ corresponding to the application of magnetic field and uniaxial stress at a temperature of 299 K are shown as color contour maps in Figs. 4(a) and 4(b), respectively. Illustrative results for the multicaloric $\Delta S$ and $\Delta T$ corresponding to the removal of magnetic field and uniaxial stress at a temperature of 317 K are shown in Figs. 4(c) and 4(d), respectively (additional data for a variety of temperatures around the transition region are shown in the Supplemental Material [47], Figs. S15 and S16).

When comparing $\Delta S$ and $\Delta T$ from single caloric effects to the values for the multicaloric effect, it is observed that significantly lower values of stress and magnetic field are required to obtain the same level of $\Delta S$ and $\Delta T$ when the two fields are combined. For instance, for the magnetocaloric effect at 299 K, a magnetic field of $\sim 2.5$ T is required to achieve $\Delta S = -14$ J kg$^{-1}$ K$^{-1}$, while a uniaxial stress of 12 MPa is applied (multicaloric effect), the magnetic field needed to obtain the same value for $\Delta S$ is as low as 1 T. With regards to $\Delta T$, a similar trend is observed. For instance, in the magnetocaloric case, for a temperature of 297 K, a magnetic field of 6 T gives rise to $\Delta T \sim 6.5$ K, while $\Delta T$ reaches 9.2 K when an additional stress of 20 MPa is applied in the multicaloric case. Such a synergic effect of dual fields also holds for the multicaloric response associated with removal of magnetic field and removal of uniaxial stress. A second remarkable outcome from the synergic response to magnetic field and uniaxial stress is observed when comparing the maximum values for the adiabatic temperature change achieved in the multicaloric effect to those corresponding to single caloric effects: within the studied range of magnetic field and uniaxial stress, the value achieved under a dual field application ($\Delta T_{\text{max}} > 9$ K), is larger than the largest values obtained for the magnetocaloric ($\Delta T_{\text{max}} \sim 7$ K) and elastocaloric ($\Delta T_{\text{max}} \sim 5$ K) effects. It is worth noticing that the contour color maps provide a guide to flexibly select combinations of magnetic field and stress to yield a tailored caloric response.

When considering the potential of multicaloric effects for future technological applications, it is particularly relevant to compare the field-induced multicaloric response under moderate magnetic fields (in the range of 1 T, which are readily accessible using permanent magnets), to the single magnetocaloric response in the same range of applied fields. The magnetocaloric adiabatic temperature change resulting from the application (or removal) of 1 T is in the range 0.9–1.7 K. However, the combination of the application (or removal) of a moderate stress with the application (or removal) of a magnetic field, results in significantly larger values: $\Delta T = 6.5$ K at $T = 296$ K (for the application of 20 MPa and 1 T), and $\Delta T = -5.4$ K at $T = 318$ K (for the removal of 20 MPa and 1 T).

In general, the multicaloric response of a given thermodynamic system is not obtained from the sum of single caloric effects because there is a contribution from a cross-coupling term [35] which accounts for the interplay between vibrational and magnetic degrees of freedom. While there is no
FIG. 5. Cross-coupling contribution to the multicaloric isothermal entropy (a) and (c) and adiabatic temperature (b) and (d) changes corresponding to the application of magnetic field and stress at $T = 299$ K (a) and (b), and to the removal of magnetic field and stress (c) and (d).

It is worth mentioning that the cross-coupling contribution for the removal (application) of the external fields is only relevant within a certain temperature window. When the temperature ($T$) is slightly higher than the transition temperature in the absence of external fields ($T > T_t$), the cross-coupling contribution is not relevant because removal (application) of a single stimulus (magnetic field or stress) suffices to induce the martensitic transition. Conversely, at higher temperatures that are further away from the transition temperature in the absence of external fields ($T > T_t$), the cross-coupling contribution becomes significant for both processes and enhances the multicaloric response of the material.

IV. SUMMARY AND CONCLUSIONS

We have studied the multicaloric response of Ni$_{50}$Mn$_{18.5}$Ga$_{25}$Cu$_{6.5}$ subjected to the combined action of magnetic field and uniaxial stress, for which elastocaloric and magnetocaloric effects are conventional and act in a synergic manner. A proper numerical treatment of the calorimetric curves measured under selected values of magnetic field and uniaxial stress has enabled us to compute the entropy $S(T, \mu_0 H, \sigma)$ over the entire phase space within the studied field ranges (20 MPa and 6 T). We have computed the multicaloric isothermal entropy change and adiabatic temperature change for any combination of application and removal of magnetic field and stress, and we have also evidenced the contribution of the interplay between magnetic and vibrational degrees of freedom to these quantities. We have shown that the combined action of magnetic field and uniaxial stress increases the reversibility of caloric effects. It has also been shown that the maximum adiabatic temperature change that results from the multicaloric effect (above 9 K) is larger than the maximum value that can be achieved for a single caloric effect. Furthermore, the magnitude of the field needed to obtain a certain value for $\Delta S$ or $\Delta T$ is significantly lowered when a second field is applied, and it has been shown that such a reduction is predominantly due to the contribution of the cross coupling between magnetism and structure. Another advantage brought by dual-field application is the expansion of the temperature window where giant caloric effects occur, when compared to that corresponding to single caloric effects.

Present results are expected to be extrapolable to other multicaloric materials with synergic individual caloric effects, and therefore our work provides guidelines in designing...
multicaloric cooling devices using materials with synergic caloric effects.

Raw and processed data are available on request from the authors.

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