Contradictory role of the magnetic contribution in inverse magnetocaloric Heusler materials

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In this paper, we illustrate the dilemma of inverse magnetocaloric materials using the example of Heusler alloys. For such materials, the magnetic and lattice contribution to the total entropy change are competing with each other. For the two paradigmatic Heusler systems of Ni-Mn-In and Ni-Mn-In-Co, we provide a systematic comparison of experimental data under different magnetic fields and hydrostatic pressures with magnetic and the magnetocaloric properties obtained from the Heisenberg model. This allows us to separate the lattice and the magnetic contribution to the total entropy of the martensitic transition. Our analysis reveals that a large magnetization change is parasitic, but at the same time it is necessary to drive the magnetocaloric effect. This contradicting role of the magnetic contribution—the dilemma—is a general characteristic of inverse magnetocaloric Heusler materials.

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I. INTRODUCTION

One prerequisite for the successful implementation of magnetic refrigeration is the applicability of materials showing large magnetocaloric effects [1–4]. The total entropy change of the magnetostructural transition ΔS_t in Gd₅(Si,Ge)₄ [5,6], La-Fe-Si [7,8], Mn₃Ga-based materials [9,10], Fe₂P-type materials [11,12], Fe-Rh [13,14], or Heusler alloys [15–17] is widely described as the sum of the following contributions:

$$\Delta S_{\rm t} = \Delta S_{\rm lat} + \Delta S_{\rm mag} + \Delta S_{\rm el},\tag{1}$$

namely the entropy change of the lattice ΔS_{lat} , of the magnetic ΔS_{mag} and of the electronic system ΔS_{el} . Recently, an intense discussion about the separation of these contributions to the magnetocaloric effect in the different first-order materials started [18–20]. Kihara *et al.* [18] experimentally demonstrated that in Heusler alloys the electronic contribution is negligibly small whereas the lattice contribution plays the dominant role.

In this paper, we further develop the idea of separating the different contributions to a general and systematic description of the whole Heusler material family instead of discussing only one single composition as often done in literature. By feeding our experimental results into a phenomenological description based on the Heisenberg model, the contradicting role of the magnetic contribution becomes apparent. It should be maximized on the one hand, but at the same time a large magnetization change deteriorates the achievable magnetocaloric effect. This we denote as the dilemma of inverse magnetocaloric materials.

We selected the ternary and quarternary Heusler systems $Ni_{50}Mn_{50-x}In_x$ and $Ni_{45}Mn_{50-x}In_xCo_5$ showing large magnetocaloric effects at the magnetostructural transition between paramagnetic martensite and ferromagnetic austenite [21]. In these materials, the martensitic transition temperature can be controlled by changing the ratio between Mn and In. This allows us to deliberately "switch off" the contribution of the magnetic subsystem to the entropy change, since at low temperatures the martensitic transition is accompanied by

a strong magnetic transition (magnetostructural transition), but at higher temperatures only the structural transformation remains. Furthermore, the partial substitution of Ni by Co leads to a systematically increased Curie temperature of the austenitic phase, resulting in an enhanced magnetization near room temperature in contrast to the Co free system [22]. In this paper, we demonstrate that the entropy change as a function of temperature of the entire material class collapses to a single line, which can already be predicted by a simple Heisenberg model description.

II. EXPERIMENTAL DETAILS

Samples of Ni-Mn-In and Ni-Mn-In-Co were prepared by arc melting and subsequent annealing at 1173 K for 24 hours. The stoichiometry was characterized using inductively coupled plasma-optical emission spectrometry (ICP-OES). Magnetic measurements were carried out using commercial MPMS-5S, PPMS 14 and LakeShore VSM systems. Pressuredependent magnetic measurements were performed using a pressure cell CC-Spr- Φ 8.5-MC4 model 1.3 GPa from Quantum Design. For the experimental determination of the entropy change a differential scanning calorimeter (DSC200 F3 Maia) with a heating and cooling rate of $\frac{\partial T}{\partial t} = 10$ K min⁻¹ was used. The adiabatic temperature change ΔT_{ad} was determined directly as described elsewhere [23].

The magnetization curves M(T) of different Co free and Co containing compositions under cooling and heating, measured in a magnetic field of 1 T, are plotted in Figs. 1(a) and 1(b). The Curie temperature $T_{\rm C}^{\rm A}$ of the austenitic phase is independent from the ratio of Mn and In of these Heusler compounds [24]. We found that there are two envelopes of the magnetization, which correspond to the saturation magnetization of pure austenite (dashed line) and martensite (dotted line). The boundary lines were fitted by the Landau theory approach proposed by Kuz'min [25]. For Ni-Mn-In in Fig. 1(a), the calculated temperature dependence of magnetization in 1 T is in very good agreement with the measurements. The magnetostructural transition between martensite and austenite can only take place in between the boundary lines of the two phases. Even though $T_{\rm C}^{\rm A}$ does not change by varying the Mn to In ratio, it is worth noting that the Curie temperature is

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FIG. 1. *M*-*T* dependences of various Ni-Mn-In (a) and Ni-Mn-In-Co samples (b) measured in $\mu_0 H = 1$ T, both for heating and cooling. The dashed and the dotted lines are calculated curves of the saturation magnetization in 1 T of austenite and martensite.

sensitive to atomic disorder, which strongly depends on the specific conditions of the heat treatment [26,27]. Furthermore, a slight variation of the Co content in Ni-Mn-In-Co leads to a deviation of the Curie temperature as well. Therefore, a comparison with values from the literature should always be done with care.

In the following, the magnetocaloric properties of the different compounds will be discussed. The entropy change of the complete transformation ΔS_t can be determined from DSC measurements by integration of the heat flow at the transition

$$\Delta S_{\rm t} = \int_{A_s}^{A_f} \frac{1}{T} \cdot (\dot{Q} - \dot{Q}_{\rm baseline}) \cdot \left(\frac{\partial T}{\partial t}\right)^{-1} dT, \qquad (2)$$

where A_s and A_f are the austenite start and finish temperatures and \dot{Q} is the heat flow per mass unit which needs to be corrected by the baseline $\dot{Q}_{\text{baseline}}$. The resulting ΔS_t values of eight different compounds are shown as solid symbols in Fig. 2. Furthermore, the diagram was amended by data from the literature which are plotted as open symbols [18,22,28–30]. One can see that above T_C^A , the entropy change of the transition is unchanged but below the Curie temperature it decreases.

III. RESULTS AND DISCUSSION

A. Temperature-dependent contributions to the entropy change

For an inverse magnetocaloric material the magnetization increases under heating during the transformation. If the low



FIG. 2. Measurements of the entropy change of the transition of Co free (a) and Co containing samples (b) obtained by DSC. The maximum entropy change of the complete transition ΔS_t from Eq. (3) of the two systems is plotted in dashed lines. For selected samples of each system, the isothermal entropy change ΔS_T (orange) and the adiabatic temperature change ΔT_{ad} (blue) in a magnetic field change of 2 T are shown as bars.

temperature state is paramagneticlike in Ni-Mn-based Heusler systems, the entropy of the magnetic system must decrease leading to a negative ΔS_{mag} . For Heusler alloys the electronic contribution to the entropy is considered as negligible as discussed by Kihara *et al.* [18]. Since ΔS_t is positive, the lattice and the magnetic contribution of the entropy change directly compete with each other.

The compositional changes of the different samples are rather small. We therefore assume for the sake of simplicity that the lattice entropy is approximately constant in the temperature range of interest.¹ We also neglect contributions arising from the coupling between the different degrees of freedom, such as electron-phonon or magnon-phonon coupling. We consider these of minor importance for the present discussion, as they are expected to be small compared to the entropy change induced by the structural transition. At temperatures above the $T_{\rm C}^{\rm A}$ of austenite, the magnetization term has no effect in zero field. Here, we can obtain the lattice entropy change $\Delta S_{\rm lat} = 46 \, {\rm J \, kg^{-1} \, K^{-1}}$ for Ni-Mn-In and 55 ${\rm J \, kg^{-1} \, K^{-1}}$ for Ni-Mn-In-Co.

Under these prerequisites, the temperature dependence of ΔS_t below T_C^A can be understood in terms of the Heisenberg

¹In fact, from a Debye model with realistic Debye temperatures of $\Theta_D = 290$ K for martensite and $\Theta_D = 250$ K for austenite, ΔS_{lat} is actually reduced by 10% at T = 200 K, compared to the high temperature limit, which does not change our argument.

model. We exploit in addition that for $T > T_{\rm C}^{\rm M}$ the magnetic entropy of the martensite holds in the entire temperature range. This means that the temperature dependence of $\Delta S_{\rm mag}$ is solely determined by the austenite magnetization M(T). Within the mean field approximation one obtains the following expression for the magnetic entropy $S_{\rm mag}$ (e.g., Ref. [31]) for $T < T_{\rm C}^{\rm A}$:

$$S_{\text{mag}}(T) = N_{\text{mag}} k_{\text{B}} \left[\ln \left(4\pi \frac{\sinh(x)}{x} \right) - x \coth(x) + 1 \right]$$

$$x = \frac{m_0 \,\mu_0 \left(\rho \, n_W \, M(T) + H \right)}{k_{\text{B}} T}.$$
 (3)

Here, N_{mag} is the number of magnetic degrees of freedom contributing to the entropy change, while m_0 is the effective magnetic moment per degree of freedom, and n_W is the molecular field constant. For a system with one magnetic species, n_W is directly related to the effective magnetic exchange parameter J_0 [32], which can be obtained from density functional theory (DFT) calculations [33]. H is the external magnetic field, ρ the mass density, and μ_0 the permeability of vacuum. The In atoms only exhibit a rather small induced moment, which originates from the hybridization with the surrounding sites. It was demonstrated for Ni₂MnGa that the magnetic moments of the Ni atoms are induced by the magnetization of the surrounding Mn atoms as well [34]. Therefore, these two species do not contribute to the entropy change and N_{mag} accounts only for the Mn and Co moments. The experimentally measured temperature dependence of magnetization M(T) in different magnetic fields is fitted by using Kuz'min's approach [25]. By this the zero-field magnetization curves as well as the effective magnetic moments are estimated. We obtain $m_0 = 4.38 \ \mu_{\rm B}$ for Ni-Mn-In and $m_0 = 4.02 \ \mu_B$ for Ni-Mn-In-Co. Taking this into account, we yield a perfect description of the experimental $\Delta S_{\rm t}$, as shown by the dashed curves in Fig. 2, with $n_W = 260$ for both Ni-Mn-In and Ni-Mn-In-Co. This value is furthermore consistent with the composition weighted average of J_0 for the different lattice sites and atomic species obtained from the DFT calculations described in Ref. [33].

As can be seen in Fig. 2, the coincidence in both Heusler systems is reasonable. A kink is visible in the ΔS_t at 398 K for the system with Co and at 314 K without Co which is related to the corresponding Curie temperature $T_{\rm C}^{\rm A}$ due to the vanishing magnetization. These values are in agreement with results from literature [22,35,36]. From Eq. (3) the cause for the reduction of the entropy change with decreasing transition temperature becomes apparent as illustrated in Fig. 2. With increasing saturation magnetization of the austenite at decreasing temperatures the magnetic contributions compete with the lattice entropy change. On the other hand, a large difference in magnetization between martensite and austenite is essential for driving the magnetocaloric effect, since an external magnetic field stabilizes the phase with higher magnetization. A large ΔM results in a huge shift of the transition temperature. Consequently, smaller magnetic field changes are required to complete the transition. We denote the contradiction that a large magnetization change is both required and unfavorable at the same time as the dilemma of inverse magnetocaloric materials.

The dilemma becomes even more obvious when comparing the transition entropy change ΔS_t with the isothermal entropy change ΔS_T (left axis) and the adiabatic temperature change ΔT_{ad} (right axis) induced by a magnetic field of 2 T. This is plotted in Fig. 2 for selected samples as bars. The ΔS_T results were determined from isofield magnetization curves up to 2 T applying the Maxwell relation. The adiabatic temperature change ΔT_{ad} was measured directly in discontinuous protocol. For instance the one Co-free compound transforming around 300 K has a potential entropy change ΔS_t of about $38 \text{ J kg}^{-1}\text{K}^{-1}$. But in a magnetic field of 2 T only half of it can be accessed. Also the ΔT_{ad} is much smaller in comparison to the other materials with a lower transition temperature. The reason for this is that the shift of the transition temperature in magnetic fields is too small to completely transform the material in 2 T, which is different for the other compounds. For the sample with a transition above the Curie temperature T_C^A [see Fig. 2(a))], nearly no magnetocaloric effect can be obtained in a magnetic field change of 2 T.

From Fig. 2 it can also be seen that the entropy change ΔS_t (plotted as dashed lines) goes to zero at a certain temperature. At this special point, the magnetic and the lattice contribution compensate each other, which we denote as the compensation temperature T_{comp} . In zero field we found $T_{\text{comp}}(H = 0)$ to be 214 K for the Co free and 228 K for the Co containing system. What would happen if the transition temperature could be shifted below the compensation temperature? In this case the entropy change of the transition ΔS_t would change sign and the inverse magnetocaloric effect of the martensitic transformation would change into a conventional one. In fact, such a change of the nature of the transformation is not observed in these Heusler alloys. However, the martensitic transition comes to a standstill. We interpret this phenomenon as the so-called kinetic arrest effect [37-41], and below the compensation point $T_{\rm comp}$ the transition is arrested.

B. Magnetic-field dependence

Magnetic measurements up to 14 T have been performed on the sample with the composition Ni_{45.7}Mn_{36.6}In_{13.5}Co_{4.2} [42] and are shown in Fig. 3. This particular sample is also plotted in Figs. 1(b) and 2(b). The transition is shifting to lower temperatures with increasing magnetic field, but especially in fields above 4 T, this shift is far from being linear as often assumed in literature [43]. In the high field range, the transition becomes increasingly suppressed because in a slightly inhomogeneous sample all parts with a transition temperature below T_{comp} cannot transform anymore. This is the reason for the increasing magnetization at low temperatures in the different magnetic fields. In 10 T only a small amount of the sample is allowed to transform into martensite, and finally in 14 T we do not observe a transition anymore, even when cooling down to 10 K (not shown).

Moreover, the increasing thermal hysteresis and transition width in magnetic fields as illustrated in Fig. 3 can be explained based on the model which was introduced above. For this purpose the Clausius-Clapeyron equation

$$\frac{dT_{\rm t}}{\mu_0 dH} = -\frac{\Delta M}{\Delta S_{\rm t}} \tag{4}$$



FIG. 3. Magnetization versus temperature of the compound $Ni_{45.7}Mn_{36.6}In_{13.5}Co_{4.2}$ in magnetic fields up to 14 T.

will be applied. From this it is possible to evaluate the shift of the transition temperature in magnetic fields for the whole material system as a function of the transition temperature, which is shown in Fig. 4. Therefore, the fitted magnetization data and the corresponding ΔS_t calculated by Eq. (2) in 0 and 2 T are used. Each solid data point corresponds to a different sample. Moreover, data from literature is added as open symbols [22,26,28–30,35,44–46]. The value $\frac{dT_t}{\mu_0 dH}$ was determined from low field M(T) curves. The two solid lines represent $-\frac{\Delta M(T,H)}{\Delta S_t(T,H)}$ in zero field for Ni-Mn-In and Ni-Mn-In-Co. Above the Curie temperature, no shift of the transition can be observed because the sample is paramagnetic. When applying a magnetic field of 2 T (dashed lines in Fig. 4) the alignment of magnetic moments causes a small shift of the martensitic transformation even above the Curie temperature.

In the low temperature regime, $\frac{dT_{\rm t}}{\mu_0 dH}$ diverges at the compensation temperature $T_{\rm comp}$. This effect explains the superlinear shift of the transition which is due to the increasing



FIG. 4. Shift of transition temperature of Ni-Mn-In (squares) and Ni-Mn-In-Co (circles) determined from experiment data (literature values are plotted as open symbols). The dashed and solid lines represent $\frac{\Delta M}{\Delta S_1}$ which were determined combining Eqs. (1), (3), and (4) in magnetic fields of 0 T and 2 T, respectively.

influence of the magnetic system until it occurs that the lattice entropy change is compensated and the transformation stops.

In this context, also the increasing width of the transition and the changing thermal hysteresis can be explained. In small magnetic fields, the transition width is in the range of 10 K (see Fig. 3). This distribution of the transition temperature over the sample is mainly due to chemical inhomogeneities. Considering the curve shape of $\frac{dT_i}{\mu_0 dH}$ in Fig. 4, it means that parts of the sample which transform at lower temperatures experience a larger change of their transition temperature than parts with a higher transition temperature. This spreading increases with the magnetic field causing a broadened transition.

The same idea can be applied in order to explain the increasing hysteresis. From Fig. 3 it can be seen that the thermal hysteresis accounts to 10 K in small fields. The difference in $\frac{dT_i}{\mu_0 dH}$ for this temperature span is rather small. By increasing the field further, the difference grows. Therefore, the martensite [cooling branch of M(T)] appears to shift more than the transformation into austenite [heating branch of M(T)].

This general tendency can also be seen in Fig. 1 for the different alloys. Both the thermal hysteresis and the transition width get broader at lower temperatures. This suggests that the intrinsic mechanism discussed above for shifting the transition temperature by magnetic fields also applies when varying the chemical composition. Despite the fact that the width of the transformation and the thermal hysteresis are also subject to extrinsic factors like sample size, grain size, and heat treatment it can be concluded that with decreasing transition temperature samples will always show broader transformations and thermal hysteresis due to the growing influence of the magnetic entropy change and the increasing shift of the transition in a magnetic field. Please note that our discussion does not yet account for a contribution from a coupling between magnetic and lattice degrees of freedom, which was recently proposed by Stonaha et al. based on the observation of a redshift of the vibrational density of states in the paramagnetic phase of Ni-Mn-In-Co austenite [47]. This contribution also increases with the magnetization change and thus aggravates the dilemma of inverse magnetocaloric Heusler alloys.

C. Pressure dependence

measurements of the Magnetic compound Ni_{45.7}Mn_{36.6}In_{13.5}Co_{4.2} under hydrostatic pressure were performed using a pressure cell. Figure 5(a) shows the magnetic behavior of this sample in a magnetic field of 1 T without pressure, in 4.5 and 8.4 kbar. One can clearly see how strong the martensitic transition is shifted to higher temperatures in the presence of hydrostatic pressure. The corresponding $\frac{dT_i}{dp}$ is in the range of 5 K kbar⁻¹ or 50 K GPa⁻¹. The magnetization of the austenite decreases under pressure, but this is in agreement with the temperature dependence of the pure austenitic phase, since the three curves in Fig. 5(a)follow the same trend in the high temperature region. This means that the influence of hydrostatic pressure on the Curie temperature of austenite T_C^A is not pronounced.

In the three different hydrostatic pressures, M(T) curves in magnetic fields from 0.2 to 2 T in steps of 0.2 T were measured in order to calculate the isothermal entropy change ΔS_T . The results are shown in Fig. 5(c) for a magnetic field



FIG. 5. (a) Magnetization as a function of temperature of Ni_{45.7}Mn_{36.6}In_{13.5}Co_{4.2} in a magnetic field of 1 T in different pressures of 0, 4.5, and 8.4 kbar. (b) Magnetization in a magnetic field of 0.2 and 2 T, in zero pressure and in 8.4 kbar. (c) Isothermal entropy change ΔS_T as a function of temperature in a magnetic field change of 1 (circles) and 2 T (triangles) under different pressure.

change of 1 (circles) and 2 T (triangles). It can be seen that the isothermal entropy change increases under pressure. It should also be pointed out that the ΔS_T peak is sharper in higher pressures. This behavior is in perfect agreement with the results discussed above (see Fig. 2). It turns out that the same trend is visible when the transition temperature is changed by means of hydrostatic pressure instead of a compositional variation. This suggests that the concept of the dilemma of inverse magnetocaloric materials also applies under the influence of pressure.

Magnetization curves in 0.2 and 2 T in 0 and 8.4 kbar are plotted in Fig. 5(b). From this comparison, it is apparent that

the thermal hysteresis is reduced under pressure by about 3 K. Furthermore, it can also be seen that the shift of the transition temperature in magnetic fields decreases from approximately -7 K T^{-1} in p = 0 kbar down to -4.5 K T^{-1} in p = 8.4 kbar. The transformation also appears to be sharper under the influence of pressure. All these findings explain why the shape of the $\Delta S_T(T)$ curves in Fig. 5(c) changes. By shifting the transition temperature about 40 K to higher temperatures simply by applying 8.4 kbar, the magnetization of the austenite phase and consequently the magnetic contribution to the entropy change decreases. This means that a larger ΔS_T can be obtained, as it illustrated in Fig. 2. At the same time, the shift of the transition temperature is reduced, which is shown in Fig. 4. The change in $\frac{dT_t}{\mu_0 dH}$ by pressure together with the sharpening of the transition and the reduction of the thermal hysteresis fits nicely into the derived concept, which demonstrates the universality of the dilemma of inverse magnetocaloric materials.

IV. CONCLUSION

In this paper, we utilized experimental data and the Heisenberg model in order to explain the temperature behavior of the transition entropy change $\Delta S_{t}(T)$ of Ni-Mn-In and Ni-Mn-In-Co. Based on this, the dilemma of inverse magnetocaloric materials becomes apparent. On the one hand, a huge change in magnetization is essential in order to drive the magnetocaloric effect. On the other hand, the large entropy change of the magnetic subsystem ΔS_{mag} being directly related to the magnetization, acts more and more against the available lattice entropy change ΔS_{lat} . As a consequence, the transition becomes arrested when both contributions compensate each other.

In addition, we demonstrated that the thermal hysteresis and transformation width increases when the transition temperature is lowered, either by magnetic field, by chemical variation or by decreasing hydrostatic pressure. The challenge for inverse magnetocaloric materials like Heusler alloys therefore is to optimize the shift of the transition temperature $\frac{dT_i}{\mu_0 dH}$ for the specific magnetic field change of the magnetocaloric refrigerator in order to utilize their full potential.

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