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Adiabatic temperature change at first-order magnetic phase transitions: $Ni_{2.19}Mn_{0.81}Ga$ as a case study

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A comprehensive study of the adiabatic temperature change ΔT_{ad} in the vicinity of a first-order magnetostructural phase transition has been carried out on a $Ni_{2.19}Mn_{0.81}Ga$ Heusler alloy. It was found that the directly measured $\Delta T_{ad} \sim 1$ K is of order of magnitude smaller than that expected from reported in the literature isothermal magnetic entropy change and specific-heat data. A new feature of the adiabatic temperature change in materials with giant magnetocaloric effect, specifically an irreversible character of ΔT_{ad} when the sample is subjected to repeatable action of magnetic field at a constant temperature, has been observed. This effect has been attributed to the irreversible magnetic-field-induced structural transformation. It has been shown that the small value of ΔT_{ad} in $Ni_{2.19}Mn_{0.81}Ga$ is not due to the kinetics of the transformation but originates from other factors which are intrinsic to first-order magnetic phase transitions. Relevance of these factors to other giant magnetocaloric materials has been outlined.

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Owing to potential applicability in room-temperature magnetic refrigeration technology, magnetocaloric effect (MCE) in magnetically ordered substances has intensively been studied during last years (see for recent reviews Refs. 1 and 2). Discovery of a giant MCE in $Gd_5(Si_{1-x}Ge_x)_4$ (Ref. 3) stimulated studies of materials undergoing first-order magnetic phase transitions. As a result, a number of other intermetallics such as MnAs and $MnFe(P_{1-x}As_x)$ based,[4,5] $La(Fe_{1-x}Si_x)_{13}$ and its hydrides,[6,7] and Heusler-based Ni-Mn-Z (Z=Ga, In, Sn) ferromagnetic shape alloys[8–10] have been reported to display attractive magnetocaloric properties. At present, it is generally acknowledged that the giant MCE observed in these materials is due to a contribution from the elastic subsystem.

Isothermal magnetic entropy change ΔS_{iso} and adiabatic temperature change ΔT_{ad} are two main parameters of MCE. ΔS_{iso} characterizes cooling capacity of the magnetic material. Although Maxwell relation $(\partial S/\partial H)_T=(\partial M/\partial T)_H$ cannot be applied, strictly speaking, in the case of first-order magnetic transitions, it has been suggested[2] that it can be used for calculation of the isothermal magnetic entropy change because the transitions are not truly discontinuous. Reported values of ΔS_{iso} in the materials with giant MCE significantly exceed that observed (for the same magnetic-field change) near Curie temperature of the prototypical magnetocaloric material Gd ($\Delta S_{iso} \approx -10$ J/kg K). For a magnetic-field change $\Delta H=50$ kOe, the isothermal magnetic entropy change $|\Delta S_{iso}| \geq 30$ J/kg K has been observed in MnAs (at $T=318$ K),[4] $La(Fe_{11.44}Si_{1.56})$ (at $T=195$ K),[11] and $Gd_5Si_2Ge_2$ (at $T=272$ K).[12] Very large values of ΔS_{iso} have been reported for a $Ni_{55.4}Mn_{20.0}Ga_{24.6}$ (at.%) single crystal ($\Delta S_{iso} \approx -86$ J/kgK at $T=313$ K),[13] polycrystalline alloys $Ni_{2.19}Mn_{0.81}Ga$ ($\Delta S_{iso} \approx -66$ J/kg K at $T \approx 350$ K),[14] and Cu-doped $Ni_2Mn_{0.75}Cu_{0.25}Ga$ ($\Delta S_{iso} \approx -64$ J/kg K at $T=308$ K).[10] It is worth noting, however, that ΔS_{iso} estimated from the Maxwell relation is presumably sensitive to the numerical integration method. Indeed, calculations of the isothermal magnetic entropy change in $Ni_{2.19}Mn_{0.81}Ga$ (Refs. 14 and 15) yield quite dissimilar results [$\Delta S_{iso}=-15$ J/kg K (Ref. 15) and $\Delta S_{iso}=-27.7$ J/kg K (Ref. 14)] despite the same transition temperature ($T \approx 350$ K) and a similar magnetic-field change ($\Delta H=18$ and 20 kOe, respectively).

In sharp contrast with the very large ΔS_{iso}, the adiabatic temperature change ΔT_{ad} in materials with the giant MCE appeared to be comparable or even smaller than that observed in Gd ($\Delta T_{ad} \approx 10$ K for the magnetic-field change

$\Delta H=50$ kOe). It has also been noted that the adiabatic temperature change measured by a direct method in $La(Fe_{13-x}Si_x)$ (Ref. 7) and $Gd_5Si_2Ge_2$ (Ref. 16) is 30%–50% smaller as compared to that calculated from isothermal magnetic entropy change and specific-heat data. Gschneidner *et al.*[17] proposed that in the case of first-order magnetic transitions the kinetics of the simultaneously occurring structural transformation can be not fast enough to follow a sweep rate of the applied magnetic field.

Because of a small volume change at the transition and high lattice coherence, the kinetic of thermoelastic martensitic transformations is fast. This implies that the ferromagnetic shape memory alloys are good candidates for the use in magnetic refrigeration technology. Moreover, for the $Ni_{2.19}Mn_{0.81}Ga$ composition, the estimation of ΔT_{ad} from temperature dependencies of total entropy change in zero and nonzero magnetic fields, $S(T)_0$ and $S(T)_H$, respectively, points to the adiabatic temperature change as large as ~ 10 K for the magnetic-field change $\Delta H=20$ kOe. Here, $S(T)_0$ was calculated from a temperature dependence of the specific heat C_p measured in zero magnetic field,[18] whereas $S(T)_H$ was determined by summing (isothermally) up the calculated $S(T)_0$ and the ΔS_{iso} reported in Ref. 14.

Motivated by these reasons, we undertook a comprehensive study of ΔT_{ad} in this compound. Results of our study have revealed, however, that directly measured ΔT_{ad} is of order of magnitude smaller than that expected from the calculation. In this work we discuss the origin of this discrepancy and show that experimentally measured ΔT_{ad} crucially depends on the relative difference between virtual Curie temperature of the low-temperature ferromagnetic phase T_C^M, and the temperature at which structural transformation to the high-temperature paramagnetic phase is observed. Besides, we report on a new feature in magnetocaloric properties of the materials undergoing first-order magnetic phase transitions. Specifically, we disclose that in the $Ni_{2.19}Mn_{0.81}Ga$ Heusler alloy the adiabatic temperature change ΔT_{ad} has an irreversible character in the vicinity of the first-order magnetostructural phase transition when the sample is subjected to repeatable action of the magnetic field at a constant temperature.

A polycrystalline $Ni_{2.19}Mn_{0.81}Ga$ sample was prepared by a conventional arc-melting method. It was annealed at 1100 K for 9 days and quenched in ice water. Metallographic observation showed that the sample is chemically homogeneous. Differential scanning calorimetry revealed that the direct martensitic transformation characterized by martensite start (M_s) and martensite finish (M_f) temperatures begins at $M_s=338$ K and ends at $M_f=329$ K. Characteristic temperatures of the reverse martensitic transformation (austenite start A_s and austenite finish A_f) was found to be $A_s=338$ K and $A_f=348$ K. Magnetization measured by a vibrating sample magnetometer showed a sharp change at the magnetostructural phase transition temperature T_{MS}. This temperature was found to be 340 K upon heating and 336 K upon cooling. Direct measurements of the adiabatic temperature change ΔT_{ad} were performed by an experimental setup described in Ref. 1. The temperature of the sample was monitored with an accuracy better than ± 0.02 K by a Copper-Constantan thermocouple, which was in direct contact with the sample. During the measurements, target temperature was approached without overheating/overcooling. Coils of the electromagnet used in our work have low inductivity, which allowed us to apply a magnetic field $H=18.5$ kOe with sweep rates up to 30 kOe/s.

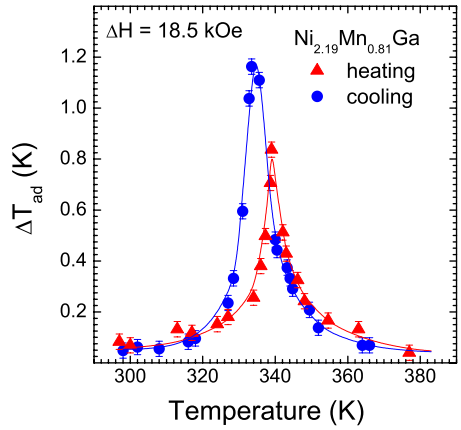

FIG. 1. (Color online) Temperature dependencies of the adiabatic temperature change ΔT_{ad} in $Ni_{2.19}Mn_{0.81}Ga$ measured upon heating and cooling. The magnetic field was applied at a sweep rate of 20 kOe/s.

Temperature dependencies of ΔT_{ad} measured upon heating and cooling are shown in Fig. 1. It is seen that the adiabatic temperature change exhibits a peak with a maximal value $\Delta T_{ad} \approx 0.8$ K at 339 K upon heating and $\Delta T_{ad} \approx 1.2$ K at 334 K upon cooling. The hysteresis in the peak value of ΔT_{ad} is due to the first-order character of the magnetostructural phase transition.

The difference in the peak values of ΔT_{ad} measured upon heating and cooling (Fig. 1) is caused by the release of latent heat of the transformation during exothermic process (austenite $\rightarrow$ martensite transformation). Considering the ΔT_{ad} vs T curve measured upon heating it is evident that at a temperature in the phase transition region, $A_s<T<A_f$, contribution of the structural subsystem to the adiabatic temperature change is unlikely to be expected in $Ni_{2.19}Mn_{0.81}Ga$ due to a low sensitivity of the phase transition temperature to the magnetic field ($\Delta T/\Delta H=0.8$ K/kOe).[19] Indeed, since the austenitic phase once formed at A_s temperature is thermodynamically stable down to M_s temperature, it is necessary to apply a magnetic field strong enough to shift M_s temperature up to the given $A_s<T<A_f$ temperature. For the applied magnetic field $H=18.5$ kOe, this can take place only near A_s. Therefore, the adiabatic temperature change measured upon heating (Fig. 1) can be considered as originating solely from the magnetic subsystem. When ΔT_{ad} is measured upon cooling down, application of the magnetic field at a temperature in the $M_s \geq T \geq M_f$ interval partially converts paramagnetic austenite into ferromagnetic martensite, which is accompanied by the release of the latent heat. Thus there are contributions to ΔT_{ad} from both magnetic and elastic subsystems, and the peak of ΔT_{ad} measured upon cooling is significantly higher than that measured upon heating.

Simple thermodynamic consideration indicates that the contribution from the structural subsystem to ΔT_{ad} will be irreversible at temperatures below A_s because the magnetic-

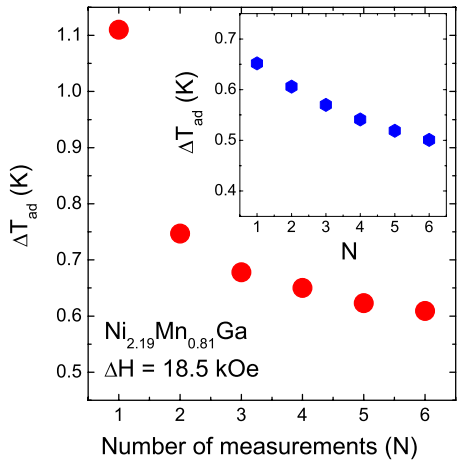

FIG. 2. (Color online) Adiabatic temperature change ΔT_{ad} vs number N of application of the magnetic field. ΔT_{ad} was measured at a constant temperature $T=336$ K after cooling the $Ni_{2.19}Mn_{0.81}Ga$ sample from high temperatures. Shown in the inset is ΔT_{ad} vs N at $T=338$ K after heating from room temperature. In both cases, the magnetic field was applied at a sweep rate of 20 kOe/s.

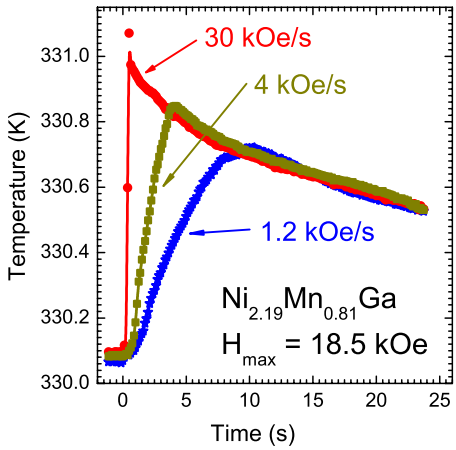

FIG. 3. (Color online) Adiabatic temperature change as a function of selected sweep rates of the applied magnetic field $\Delta H=18.5$ kOe.

field-induced martensite is stable at $T \leq A_s$. At these temperatures, the removal of the magnetic field will not convert ferromagnetic martensite back to the paramagnetic austenite and the contribution of the elastic subsystem to ΔT_{ad} will be negligible upon subsequent application of the magnetic field. For a fixed temperature, this should lead to a much smaller value of ΔT_{ad} as compared to that measured during first application of the magnetic field. Such an effect has indeed been observed in $Ni_{2.19}Mn_{0.81}Ga$ (Fig. 2). In this experiment, the sample was cooled from a high temperature $T > A_f$ down to $T=336$ K. After that, the magnetic field was applied and removed several times. It is seen from Fig. 2 that $\Delta T_{ad}=1.1$ K is observed only upon first application of the magnetic field. Upon the subsequent application of the magnetic field, ΔT_{ad} appears to be much smaller due to irreversible heat dissipation. During further cycles of application and removal of the magnetic field (Fig. 2), ΔT_{ad} slightly decreases due to quasiadiabatic experimental conditions.

The result shown in Fig. 2 is a fair indication that the kinetics of the martensitic transformation is fast enough to respond to the application of the magnetic field even for a rather high sweep rate 20 kOe/s. To make it more evident, we have measured ΔT_{ad} at various sweep rates ranging from 30 to 1.2 kOe/s. It is seen from Fig. 3 that ΔT_{ad} rapidly increases with increasing magnetic field and reaches a maximum when ΔH reaches its maximal value 18.5 kOe. After that the ΔT_{ad} gradually decreases with time. The fact that all the time dependencies of ΔT_{ad} measured in the field $H_{max}=18.5$ kOe can be extrapolated by the same function indicates that the sweep rate has no influence on adiabatic temperature change in the compound studied. The peak value of ΔT_{ad} does depend on the sweep rate because of the heat dissipation caused by the quasiadiabatic experimental conditions. A similar trend in ΔT_{ad} has recently been reported for Gd.[20] These facts indicate that adiabaticity will be a crucial problem in designing magnetic refrigerators.

In the light of our experimental results (Figs. 2 and 3) it is evident that the huge difference between calculated (≈ 10 K) and experimentally measured (≈ 1 K) ΔT_{ad} in $Ni_{2.19}Mn_{0.81}Ga$ cannot be accounted for by a slow kinetic of the martensitic transformation. In order to understand the origin of the discrepancy between calculated and experimentally measured ΔT_{ad} in $Ni_{2.19}Mn_{0.81}Ga$ it is necessary to consider specific features of first-order magnetic phase transitions. They are an abrupt change of the magnetic order, due to the structural transition, and the coexistence of ferromagnetic and paramagnetic phases in the phase transition region.

The abrupt change of the magnetic order does not necessary mean that Curie temperature of the low-temperature phase is equal to the transition temperature. In the majority of cases this is an indication that the exchange integral of the high-temperature phase forming upon structural transformation is lower than the structural transition temperature. Accordingly, the reverse transition from the high-temperature paramagnetic to the low-temperature ferromagnetic phase occurs because the exchange integral of the low-temperature phase is higher than the structural transition temperature. Actually, virtual Curie temperature of the high-temperature phase can be considerably lower than the structural transition temperature. Obviously, the impact of a magnetic field on the magnetic order parameter (hence on ΔT_{ad}) far below (virtual) Curie temperature of the low-temperature phase will be much less than near order-disorder magnetic transition temperature. Although this aspect of first-order magnetic phase transitions has already been noticed by Giguère *et al.*,[16] it has not received due attention so far.

In the case of $Ni_{2+x}Mn_{1-x}Ga$ system, there is solid evidence[21] that the virtual Curie temperature of the low-temperature martensitic phase T_C^M in $Ni_{2.19}Mn_{0.81}Ga$ is ~ 30 K higher than the magnetostructural phase transition temperature T_{MS}. Besides, estimations[19,21,22] of the relative strength of exchange interactions in the martensitic and austenitic phases have indicated that T_C^M is at least 40–50 K higher than the virtual Curie temperature of the high-temperature austenitic phase T_C^A. This suggests that T_{MS} of $Ni_{2.19}Mn_{0.81}Ga$ is between T_C^A and T_C^M. Since the magnetic

field has a weak influence on the magnetic order parameter far below (above) T_C^M (T_C^A) temperature, the experimentally measured adiabatic temperature change in $Ni_{2.19}Mn_{0.81}Ga$ is much smaller than that calculated from isothermal entropy change[14] and specific heat[18] data.

Another factor that affects the value of the directly measured ΔT_{ad} is that in the transition region the system is structurally and magnetically inhomogeneous, consisting of ferromagnetic low-temperature phase and paramagnetic high-temperature phase. If exchange integral of the high-temperature phase is well below this region, a fraction of the paramagnetic phase will not contribute to ΔT_{ad} and will act as a parasitic loading. For example, in the system consisting of equal fractions of the ferromagnetic and paramagnetic phase (assuming that they have the same thermal properties), the effective adiabatic temperature change ΔT_{ad} measured experimentally will be two times lower than that provided by the magnetic subsystem. Considering the low sensitivity of the T_{MS} temperature to the magnetic field and that T_C^A is fairly below T_{MS} in $Ni_{2.19}Mn_{0.81}Ga$, it is likely that the magnetic inhomogeneity is a factor of vital importance for the adiabatic temperature change ΔT_{ad} in this compound.

In conclusion, we argue that the above remarks on the adiabatic temperature change at first-order magnetic phase transitions are crucial for all materials with giant MCE. It is evident from the above discussion that exchange integrals of low- and high-temperature phases, temperature hysteresis of first-order magnetic phase transitions, and sensitivity of the magnetostructural phase transition temperature to the magnetic field are critical factors, which, alongside with the kinetics of the transition, determine magnetocaloric properties of materials undergoing first-order magnetic transitions.

The impact of the magnetic field on magnetostructural phase transition and temperature hysteresis of the transformation can be easily determined from magnetization measurements. Virtual Curie temperature T_C of the low-temperature phase can be estimated from temperature dependence of effective ferromagnetic spin stiffness constant, $D=D_0\sqrt{1-T/T_C}$, which can be determined, e.g., from neutron diffraction measurements.[23] To shed light on the kinetics of first-order magnetic phase transitions, it is instructive to compare magnetization curves measured, at the same temperatures and on the same samples, under near equilibrium (steady magnetic field) and nonequilibrium (impulse magnetic field) conditions.

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