



An indirect approach based on Clausius–Clapeyron equation to determine entropy change for the first-order magnetocaloric materials



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ABSTRACT

Taking into account the phase fraction during the structural transition for the first-order magnetocaloric materials, an improved isothermal entropy change (ΔS_T) determination has been put forward based on the Clausius–Clapeyron (CC) equation. It was found that the ΔS_T value evaluated by this method is in excellent agreement with those determined from the Maxwell relation (MR) using magnetic measurements for some Heusler alloys with a weak field-induced phase transforming behavior, such as Ni–Mn–Sn Heusler alloys. In comparison with the MR based on isofield magnetization measurements (MRIF), this method is very convenient to obtain the ΔS_T derived from only few thermomagnetic curves. More importantly, it is quite superior to the MR-based method in eliminating the overestimation of ΔS_T due to the appearance of the spurious spike derived from MR employing isothermal magnetization measurements (MRIT).

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1. Introduction

The magnetocaloric effect (MCE), which reflects the magnetoresponsive ability of refrigerating when a magnetic material is submitted to the external magnetic field variations, has emerged as an attractive option in the new generation of energy-efficient cooling technologies. Since the discovery of pseudo-binary $\text{Gd}_5\text{Si}_2\text{Ge}_2$ compound by Pecharsky and Gschneidner in 1997 [1], the MCE became a promising contender to the conventional vapor-compressive refrigerating methods under ambient conditions due to its environmental friendliness, higher cooling efficiency and compactness. Since then, the giant MCE has also been extensively studied in other intermetallic compounds, such as $\text{MnAs}_{1-x}\text{Sb}_x$ [2], $\text{MnFeP}_{1-x}\text{As}_x$ [3], $(\text{Mn,Fe})_2\text{P}_{1-x}\text{Si}_x$ [4], $\text{La}(\text{Fe}_{1-x}\text{Si}_x)_{13}$ hydrides [5,6], and the family of Heusler alloys like Ni–Mn–Ga [7] and Ni–Mn–Z (Z = In, Sn, Sb) [8]. Among these materials, the outstanding MCE is due to the involvement of latent heat produced by structural transition in combination with magnetic ordering and changes in the electronic band structure. In general, for the materials with direct MCE, both the lattice entropy change (ΔS_L) and magnetic entropy change (ΔS_{mag}) contribute positively to the total measured MCE [9]. Whereas for the materials with inverse MCE, the magnetocaloric response comes from the ΔS_L , and the ΔS_{mag}

plays a negative role [10,11]. Thus, entropy change associated with the first-order magnetostructural phase transition (FOMT) tends to be much more complicated than the second-order, i.e., purely magnetic transition.

As is well known, the characteristic parameters for a magnetocaloric compound are the isothermal entropy change (ΔS_T) and the adiabatic temperature change (ΔT_{ad}) when a magnetic field is applied or removed. To fully exploit the MCE for a given material, it is essential to clarify the evolution of ΔS_T or ΔT_{ad} with temperature and magnetic field. Usually, determining the ΔT_{ad} with direct or quasi-direct calorimetric methods is difficult and challenging. Therefore, the simplest and most widely used experimental approach has been put forward, i.e., the ΔS_T can be derived from Maxwell relation with a numerical form using isothermal magnetization measurements (denoted as MRIT here)

$$\Delta S_T = \int_{H_1}^{H_2} \frac{\partial M}{\partial T} dH \approx \sum \frac{M_{i+1} - M_i}{T_{i+1} - T_i} \Delta H. \quad (1)$$

However, the MRIT has encountered some challenges during the last two decades. For example, a large experimental discrepancy led Giguère et al. [12] to claim that, rather than the MRIT, the Clausius–Clapeyron (CC) equation should apply to calculate the MCE associated with FOMT, since its magnetization curve is not a continuous, derivable function. Soon after, Gschneidner et al. [13] argued that the discrepancy just originates from kinetic

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effect. Meanwhile, Sun et al. [14] also pointed out that CC equation is just a special case of integrated Maxwell relation and is inadequate to evaluate the ΔS_T value for an incomplete transformation. Particularly, recent progress on the inverse MCE research for Ni–Mn–Sn alloys aroused a new round of argument once again. Zou et al. [15,16] claimed that the ΔS_T value is seriously overestimated by MRIT in $\text{Ni}_{43}\text{Mn}_{46}\text{Sn}_{11}$ due to the occurrence of a magnetically inhomogeneous martensitic state. On the contrary, Mañosa et al. [17] proved that the ΔS_T values respectively obtained from MRIT and calorimetric measurements are in well agreement for $\text{Ni}_{50}\text{Mn}_{35}\text{Sn}_{15}$. Despite the validity and generality of MRIT being still under debate, it is undeniable that the direct application of MRIT would lead to some unphysical results. In most cases, a “spike” is always observed on the $\Delta S_T(T)$ curve, especially in some materials with a pronounced field-induced transition [2,18–22]. A spike value for $\text{Mn}_{0.997}\text{Fe}_{0.003}\text{As}$ unexpectedly attains up to ~ 320 J/kgK for a field change of 5 T under the ambient pressure [23]. This value is far above those reported for all known magnetocaloric materials as well as the theoretical prediction. Such a “colossal” MCE can be attributed to the incorrect application of MRIT, which gives rise to a spurious artifact. In fact, some practical methods to modify the ΔS_T values obtained from MRIT have been proposed by Liu et al. [24] and Cui et al. [25]. Nevertheless, the former one was found to be inadequate for an extreme case of $\text{Mn}_{0.99}\text{Cu}_{0.01}\text{As}$ [26], while the latter one is very complex for the practical use. In addition to MRIT, the ΔS_T can be also determined accurately by using Maxwell relation based on isofield magnetization measurements (referred to as MRIF here) [27], but this method needs a large number of thermomagnetic curves with great measuring cost. In the present work, a proper method based on the CC equation using isofield magnetization measurements (CCIF) has been proposed to estimate the realistic MCE for the magnetocaloric materials with FOMT. The feasibility of this method was tested on the $\text{Ni}_{43}\text{Mn}_{46}\text{Sn}_{11}$, $\text{Ni}_{50}\text{Mn}_{35}\text{Sn}_{15}$ and $\text{Ni}_{45}\text{Co}_5\text{Mn}_{36.6}\text{In}_{13.4}$ Heusler alloys with their inverse MCE, as well as MnAs and $\text{Gd}_5\text{Si}_2\text{Ge}_2$ compounds with direct MCE. All these experimental results demonstrate that such a new method using to evaluate the ΔS_T is superior to the MR-based method.

2. Experimental

Nominal stoichiometry $\text{Ni}_{43}\text{Mn}_{46}\text{Sn}_{11}$ and $\text{Ni}_{50}\text{Mn}_{35}\text{Sn}_{15}$ ingots were prepared by arc melting high-purity Ni, Mn, Sn metals under an argon atmosphere. After melting, the samples were sealed in evacuated quartz tubes in order to homogenize at 1173 K for 24 h, and then subsequently quenched in ice-water. Their crystal structures and phases were verified by the X-ray diffraction (Rigaku, Ultima IV) using $\text{Cu } K_\alpha$ radiation. The results show that both the $\text{Ni}_{43}\text{Mn}_{46}\text{Sn}_{11}$ and $\text{Ni}_{50}\text{Mn}_{35}\text{Sn}_{15}$ samples are single phase with a $L2_1$ cubic structure (austenite phase) at room temperature. The magnetic characterizations were carried out by a Quantum Design VersaLab magnetometer (VersaLab™, 3 Tesla). When dealing with the $\text{Ni}_{45}\text{Co}_5\text{Mn}_{36.6}\text{In}_{13.4}$, MnAs and $\text{Gd}_5\text{Si}_2\text{Ge}_2$ samples, the correlatively experimental data were directly extracted from previous literatures [2,22,28].

The isofield magnetization measurements were carried out as: cooling the sample down to T_- (a full martensitic state) in the absence of magnetic fields, and then the measurement was made on increasing temperature from the T_- to T_+ (a full austenitic state) with a scan rate of 1.0 K/min in the presence of magnetic field ($H, T_- \rightarrow T_+$). In this way, the isofield $M(T)$ heating curve was obtained. Subsequently, the measurement was taken on the decreasing temperature from the T_+ to the T_- without removing the magnetic field ($H, T_+ \rightarrow T_-$), and the isofield $M(T)$ cooling curve was acquired as well.

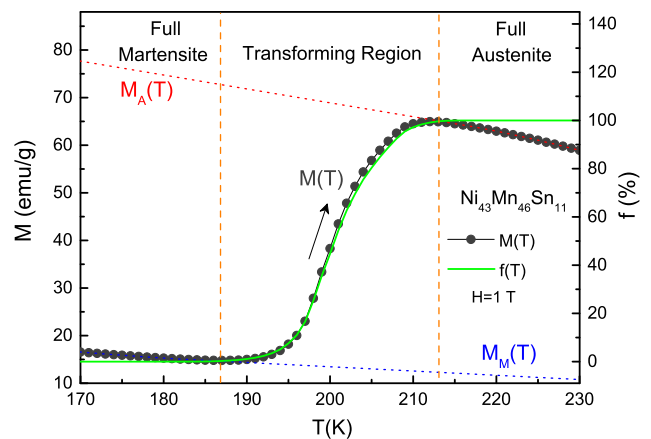


Fig. 1. The $M(T)$ curve under a static magnetic field of 1 T for $\text{Ni}_{43}\text{Mn}_{46}\text{Sn}_{11}$ sample (full circles). The red and blue dot lines represent $M_A(T)$ and $M_M(T)$ obtained by extrapolating the linear part of magnetization. The corresponding austenite fraction $f(T)$ is represented using a green solid line. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The isothermal magnetization measurements were performed as: (i) the isothermal $M(H)$ curve measured on heating mode: heating the sample at zero fields from T_- to the measuring temperature T_i without overshooting the target temperature, and then recording the isothermal magnetization $M(H)$ by scanning fields ($0 \rightarrow H, T_i$). Next, the sample was cooled back down to T_- at zero fields, and heated to the next temperature, T_{i+1} , for measuring. (ii) Isothermal $M(H)$ curve measured on cooling mode: cooling the sample down from T_+ to T_i without overshooting the target temperature, and collecting the isotherm $M(H)$ by scanning fields ($0 \rightarrow H, T_i$). Afterwards, the sample was heated up to T_+ at zero fields and cooled down to the next temperature, T_{i+1} , for measuring. Before each $M(H)$ curve measurement, the sample was carefully recovered to the initial state, since the first-order system could remain partially transformed in higher magnetization after removing the saturate field if the cooling martensitic transformation is not crossed [26,29].

3. Results and discussion

In order to illustrate the use of the CCIF method, we firstly selected the intensively studied ternary $\text{Ni}_{43}\text{Mn}_{46}\text{Sn}_{11}$ Heusler alloy as a representative. Fig. 1 shows its $M(T)$ heating curve from $T_- = 150$ K to $T_+ = 240$ K in the presence of a static field $H = 1$ T. The sample undergoes a reverse martensitic transformation from a weak-magnetic martensite to a ferromagnetic austenite phase. To our knowledge, the finite transition width is due to the inhomogeneous nature of the sample [10], and the transforming process can be supposed to be continuous. In this case, austenite phase fraction, $f(T)$, should be taken into account and it can be described by using $M(T)$ data. This is based on an assumption that the total magnetization is proportional to the phase volume fraction [10, 30–33]. It is worth noting that the kinetic arrest effect [34] which only occurs at very high fields is ignored here. In order to determine the $f(T)$, it is necessary to first obtain the magnetization of full martensite $M_M(T)$ and austenite phases $M_A(T)$, which can be roughly deduced by linearly extrapolating heating curve outside the transforming region, as illustrated by the blue/red dot lines in Fig. 1. By combining $M_M(T)$ and $M_A(T)$, the $f(T)$ can be calculated by the below expression

$$f(T) = \frac{M(T) - M_M(T)}{M_A(T) - M_M(T)}. \quad (2)$$

Following Eq. (2), the resultant $f(T)$ curve at $H = 1$ T was obtained, as indicated by the green solid line in Fig. 1.

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