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Contribution of entropy changes to the inverse magnetocaloric effect for $Ni_{46.7}Co_5Mn_{33}In_{15.3}$ Heusler alloy

Zhe Li [a,*], Yuanlei Zhang [a], Kun Xu [a], Taoxiang Yang [a], Chao Jing [b], Hao Lei Zhang [c]

[a] College of Physics and Electronic Engineering, Key Laboratory for Advanced Functional and Low Dimensional Materials of Yunnan Higher Education Institute, Qujing Normal University, Qujing 655011, PR China
[b] Department of Physics, Shanghai University, Shanghai 200444, PR China
[c] Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, PR China

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ABSTRACT

In this paper, the changes of volume fractions between austenitic and martensitic phase have been carefully deduced through magnetization data for polycrystalline $Ni_{46.7}Co_5Mn_{33}In_{15.3}$ alloy during reverse martensitic transformation at different magnetic fields. On this basis, the contributions of the lattice and the spin components to the total entropy changes could be effectively separated by using the Clausius–Clapeyron equation and the Debye theory calculations. It is concluded that the lattice contribution works against the magnetic contribution to the inverse magnetocaloric effect (MCE) in this alloy. Further analysis indicates that the effective inverse MCE comes from field-induced variation of the crystal structure. On the contrary, the change of the magnetic moment alignment in this process yields negative contribution, leading to a reduction of the total inverse MCE by about 33%.

1. Introduction

The magnetocaloric effect (MCE) arises from the entropy (or temperature) changes when a magnetic material is submitted to external magnetic field variations ΔH, and its capability can be described either by the isothermal entropy change ΔS_T or by the adiabatic temperature change ΔT_{ad} [1]. Since the discovery of the giant MCE in $Gd_5Si_2Ge_2$ [2], much attention has been focused on this kind of compounds because of their potential application for magnetic refrigeration at room temperature, such as $MnAs_{1-x}Sb_x$ [3], $MnFeP_{0.45}As_{0.55}$ [4] and $LaFe_{13-x}Si_x$ [5]. The mechanism behind the giant MCE is believed to be resulted from the spin orientation, crystallographic distortion and changes in the electronic band structure during the first order magnetostructural transformation [6].

In 2004, a new type of ferromagnetic shape memory alloys have been found in Mn rich Ni–Mn based Heusler alloys, such as Ni–Mn–X(Sn, In, Sb) [7], which also undergoes first order martensitic transformation (MT) from a high-symmetry austenitic phase to a low-symmetry martensitic phase with an abrupt drop of magnetization in the cooling process. Owing to magnetostructural coupling around MT, Krenke et al. first reported a large inverse MCE in $Ni_{50}Mn_{50-x}Sn_x$ alloys [8], and the magnitude of ΔS_T is comparable to $Gd_5Si_2Ge_2$ at the similar conditions [2]. Since then, the enhanced ΔS_T during MT was continuously obtained in other ternary and quaternary Heusler alloys by tuning compositions [9–16]. In the very recent years, Liu et al. further observed a giant inverse MCE with reverse MT in $Ni_{45.2}Co_{5.1}Mn_{36.7}In_{13}$ alloy, which is entirely contributed from the contribution of lattice entropy change ΔS_L, and they explained such phenomenon through an practical assumption, i.e., the magnetic entropy change keeps unchanged when the transformations evolves from a first order to second order (a pure magnetic transition of austenite) [17]. In order to get a deeper understanding of the giant inverse MCE, it is not trivial to directly distinguish the contributions of crystallographic modification and magnetic ordering from MT. In addition, numerous studies proposed that the size of MCE is related to the transformed phase fraction induced by a ΔH at a given temperature [17–22]. Based on this motivation, we attempted to clarify the contributions of various entropy changes from MT through transformed volume fraction by combining the Clausius–Clapeyron (C–C) equation and the Debye theory. In this work, we still took $Ni_{45}Co_5Mn_{37}In_{13}$ as an example, and investigated the evolutional trends between the ΔS_L and the magnetic entropy change ΔS_M^{str} upon reverse MT at different magnetic fields in detail. Our results demonstrate that the effective inverse MCE is only contributed from a part of ΔS_L (~77%), while the rest of ΔS_L is consumed by opposite contribution of the magnetic moment alignment during reverse MT.

* Corresponding author. Permanent Address: College of Physics and Electronic Engineering, Qujing Normal University, Sangjiang Street, Qujing 655011, P. R. China. Tel/fax: +86 8748968627.
E-mail addresses: zheli@shu.edu.cn (Z. Li), xukun0830@hotmail.com (K. Xu).

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2. Experimental details

Polycrystalline $Ni_{45}Co_5Mn_{37}In_{13}$ alloy with nominal composition was fabricated by the conventional arc-melting method. The weight loss after melting was found to be less than 1.5%. The obtained ingot was annealed in evacuated quartz capsule for 24 h at 1173 K, and it was subsequently quenched in ice water. Its real composition was determined by energy-dispersive spectrometer (EDS, Tecnai-F20, FEI) analysis corresponding to $Ni_{46.7}Co_5Mn_{33}In_{15.3}$. The crystal structure was identified by powder x-ray diffraction using a Rigaku Ultima-IV x-ray diffractometer both at 300 K and 410 K, respectively. The microstructure of the specimen was studied by optical microscopy (DM2500-M, Leica). Magnetization data were acquired using a vibrating sample magnetometer (VSM, Versalab, Quantum Design). Examination of heat capacity at low temperature using specimen with a cubic shape of about $1\times1\times1$ mm^3, was performed by physical property measurement system (PPMS-9, Quantum Design).

3. Results and discussion

Fig. 1 shows the x-ray diffraction patterns of $Ni_{46.7}Co_5Mn_{33}In_{15.3}$ alloy at different temperatures. The reflections of Fig. 1(a) indicate that the sample at 300 K has an $L1_0$-type nonmodulated martensitic structure, where $a=0.3926$ nm, $c=0.6809$ nm and $\alpha=90^\circ$. The c/a of such tetragonal structure is about 1.7343, and is comparable to that observed in $Ni_{45}Co_5Mn_{40}In_8Sn_2$ alloy [23]. In the mean time, the microstructure of sample at room temperature is also related to the pure martensitic phase, and its grain size is larger than 150 μm, as shown in the inset of Fig. 1(a). From Fig. 1(b), the reflections indicate that the sample at 410 K has an $L2_1$-type austenite structure with lattice parameters $a=0.5955$nm and $\alpha=90^\circ$. For present sample, consequently, the volume change of unit cell between two phases ($\Delta V/V_0=2.56\%$) is slightly larger than that reported in $Ni_{50}Mn_{37.5}Al_{12.5}$ alloy, probably because the atom radius of Al is significantly smaller than that of In [24].

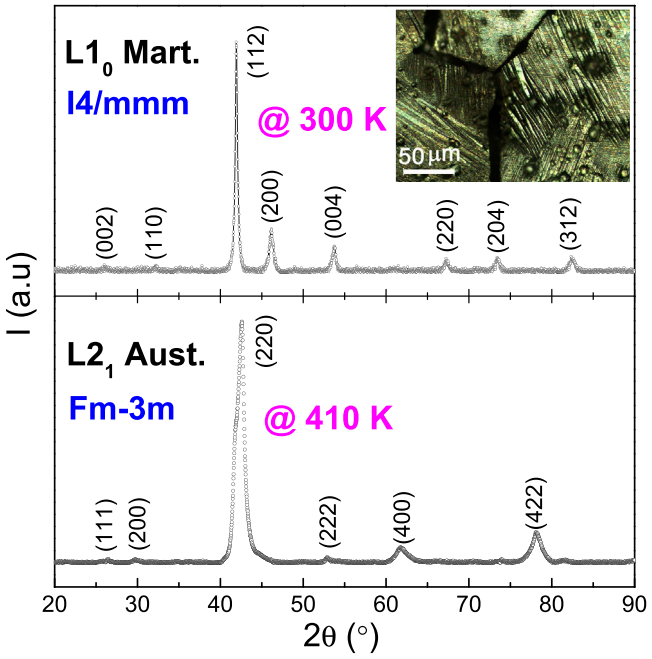

Fig. 1. (Color online) X-ray diffraction patterns of $Ni_{46.7}Co_5Mn_{33}In_{15.3}$ alloy at different temperatures. Inset: optical microscopy image of this alloy at room temperature.

Fig. 2(a) illustrates the temperature dependence of magnetization $M(T)$ curves for $Ni_{46.7}Co_5Mn_{33}In_{15.3}$ sample on cooling and heating in a magnetic field of 50 mT. When the temperature is above 380 K, a sharp change of magnetization at T_C^A appears, corresponding to a second order magnetic transition from paramagnetic (PM) austenite to ferromagnetic (FM) austenite. When the temperature lies within the range of 345–375 K, we can see that the forward and the reverse MT occur, i.e., the two transitions take place between FM and PM with an obvious thermal hysteresis, revealing a first order transition feature. Here the M_s and A_f denote martensite start temperature and austenite finish temperature, respectively. According to the previous studies [25,26], the $M(T)$ data can transform to $f(T)$, the volume fraction of austenite in the sample at a certain temperature, by assuming that total magnetization is proportional to the phase volume fraction. It is worth noting that we just consider the heating process to avoid influence of thermal hysteresis. To determine $f(T)$, it is necessary to first obtain the magnetization of pure martensite $M_M(T)$ and austenite phases $M_A(T)$ at a given temperature, which can be deduced by linearly extrapolating heating curve from transition point (A_s and A_f), as illustrated by the red dashed line in the inset of Fig. 2. By combining $M_M(T)$ and $M_A(T)$, the $f(T)$ can be calculated by the following equation:

$$f(T)=\frac{M(T)-M_M(T)}{M_A(T)-M_M(T)}. \tag{1}$$

The normalized curve $f(T)$ is plotted by the blue solid line in the inset of Fig. 2. Obviously, the shape of $f(T)$ curve follows the $M(T)$ from experimental data in the transforming range very well.

Based on the magnetization data, we also plotted the $f(T)$ curves at different magnetic fields using the same approach mentioned above, as shown in Fig. 3. For the case of our sample, it can be found that the application of a magnetic field keeps the shape of $f(T)$ curves almost unchanged, but the equilibrium temperature of reverse MT [$T_0=(A_s+A_f)/2$, denoted as pink star] significantly decreases. The magnetic field dependence of T_0, which is determined from the intersections of extrapolations from linear regions of M–T curves measured at different fields, is also presented in the inset of Fig. 3. It is clearly seen that the T_0 linearly decreases with the increasing of magnetic field. The slope of this curve (dT_0/dH) is about 3.2 K/T. Such effect suggests that volume fraction of austenite is added by an applied magnetic field at isothermal condition, which is a key fact that demonstrates why

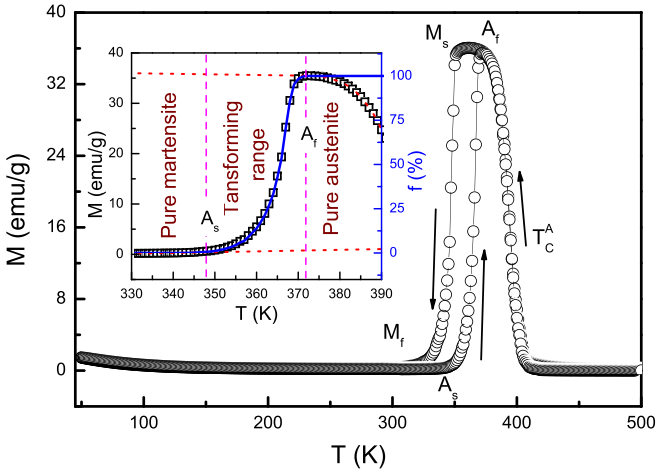

Fig. 2. (Color online) Thermomagnetic curves for $Ni_{46.7}Co_5Mn_{33}In_{15.3}$ alloy on cooling and heating procedures at 50 mT. Inset: the red dashed line shows linearly extrapolating heating curve (blank pane) from the transition point, and normalized heating curve indicates the volume fraction of austenite in the transforming range (blue solid line).