Contribution of entropy changes to the inverse magnetocaloric effect for Ni$_{46.7}$Co$_5$Mn$_{33}$In$_{15.3}$ Heusler alloy

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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$_5$Mn$_{33}$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 magnetic refrigeration at room temperature, such as Mn$_{12}$As$_{1-x}$Sb$_x$ [3], MnFe-P$_{0.45}$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 martensitic 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 magnetostuctural 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 $\Delta S_T$ is comparable to Gd$_5$Si$_2$Ge$_2$ at the similar conditions [2]. Since then, the enhanced $\Delta S_T$ 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 $\Delta S_L$, 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 $\Delta H$ 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$_{45.2}$Co$_5$Mn$_{36.7}$In$_{13}$ as an example, and investigated the evolution trends between the $\Delta S_L$ and the magnetic entropy change $\Delta S_M$ upon reverse MT at different magnetic fields in detail. Our results demonstrate that the effective inverse MCE is only contributed from a part of $\Delta S_L$ (~77%), while the rest of $\Delta S_L$ is consumed by opposite contribution of the magnetic moment alignment during reverse MT.