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Ni–Mn-based magnetic shape memory alloys: Magnetic properties and martensitic transition

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Abstract

We report a compilation of the structural and magnetic properties of Ni–Mn-based magnetic alloys with special attention to those which undergo martensitic transformations. We discuss the effect of the coupling between structure and magnetism on the properties of these alloys and how this coupling affects their martensitic transition. We show that as a consequence of such a coupling, these alloys exhibit an unusual magneto-mechanical and magneto-thermal behaviour which gives rise to singular functional properties such as magnetic shape memory and magnetic superelasticity, as well as conventional and inverse giant magnetocaloric effects.

Keywords: Ni–Mn–Ga; Ni–Mn–Sn; Ni–Mn–In; Heusler alloy; Martensitic transition; Magnetic shape memory; Magnetic superelasticity; Magnetocaloric effect

1. Introduction

The study of magnetic shape memory alloys has become a field of active research during the last decade. The coupling of magnetism and structure in such materials leads to peculiar magneto-mechanical as well as magneto-thermal behaviour that render these materials important functional materials [1]. Prominent among these properties are the magnetic shape memory effect [2] and the giant magnetocaloric effect [3].

By far, the most studied material is the Ni–Mn–Ga alloy. Large magnetic field induced strains were reported firstly for a stoichiometric Ni_2MnGa single crystal [4]. It was shown that the strain originates from the re-orientation of the martensitic domains in order to reduce the Zeeman energy [5]. Later, giant strains up to 10% were reported for non-stoichiometric single crystals [6]. In addition, this alloy also exhibits a large magnetocaloric effect [7,3], i.e., a large entropy change occurs when a magnetic field is applied isothermally. Depending on composition and magnetic field, the entropy change can be either positive or negative. This singular behaviour has been shown to be related to the length scale at which the coupling between structure and magnetism takes place [8]. The largest entropy change (entropy decrease with application of the field) occurs when the martenitic transition coincides with the ferromagnetic transition [9].

In recent years, the search for magnetic shape memory alloys other than Ni–Mn–Ga has become of great importance. Among others, the following systems have been investigated: Co–Ni–Al [10], Co–Ni–Ga [11], Ni–Fe–Ga [12] and Ni–Mn–X (with X =Al, Sn, In and Sb) [13–18].

In the Ni–Mn–X family, the magnetic moments are localized at the Mn-atoms, and their interaction is oscillatory via the conduction electrons. Hence, the magnetic behaviour of these alloys is extremely sensitive to the distance between Mn atoms such that a wide variety of magnetic behaviours are encountered for the different X atoms in the high temperature cubic phase. The Ni–Mn–Al alloy system exhibits a mixed ferromagnetic and antiferromagnetic order with the antiferromagnetic components being dominant; Ni–Mn–Ga is ferromagnetic; and Ni–Mn–Sn and Ni–Mn–In are ferromagnetic but the Mn rich non-stoichiometric compounds incorporate some antiferromagnetic components.

Such a peculiar magnetic behaviour exhibited by Ni–Mn–Sn and Ni–Mn–In gives rise to unique properties such as magnetic superelasticity [19] and the inverse magnetocaloric effect [20]. Magnetic superelasticity is the magnetic analogue of the

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superelasticity exhibited by conventional shape memory alloys under application and removal of an external stress [21]. In the magnetic case, the sample deforms and reversibly recovers by simply applying and removing a magnetic field. In this case, the shape change is not due to a re-orientation of martensitic domains (as in Ni–Mn–Ga) but to the reverse/forward martensitic transition when the field is applied/removed. The inverse magnetocaloric effect occurs when the entropy of a magnetic material increases by the isothermal application of a magnetic field. Simple thermodynamic arguments show that the material will cool down when the magnetic field is applied adiabatically.

In the present paper, we will review some of the magnetic and structural properties of Ni–Mn–X alloys which yield to the aforementioned functional properties of these materials.

2. Coupling of magnetism and structure

The coupling of magnetism and structure in magnetic materials is a dependence of the magnetic interactions on the atomic distances (structure and lattice dynamics) on the solid. The reverse effect also applies: the crystal structure and also the lattice dynamics (phonon energies and elastic constants) depend on the magnetic order. In Heusler alloys, the dependence of magnetism on the degree of atomic order has been known for many decades [22]. Most of the Heusler magnetic shape memory alloys covered in the present paper exhibit long range $L2_1$order in the cubic phase, and the diffusionless character of the martensitic transition ensures that the martensitic phase is also atomically ordered. For Ni–Mn–Al, however, long-range $L2_1$order is not fully achieved and there is a co-existence of antiferromagnetism and ferromagnetism in the ground state of this system.

Besides the aforementioned coupling, which takes place at the microscopic length scale, in martensitic materials, the existence of both structural (martensite variants) and magnetic domains enables the coupling of magnetism and structure to show up at a mesoscopic scale.

The microscopic coupling modifies the relative stability of the two crystallographic phases, and it is responsible for the shift in the martensitic transition temperature with application of magnetic field. By contrast, the coupling at a mesoscopic scale is expected to have an influence on the kinetics of the martensitic transition. The relative strength of the magneto-structural coupling at the different length scales depends on the particular alloy system and also on composition. It is expected that mesoscopic effects will be dominant for those alloys with strong magnetic anisotropy and a weak change in the saturation magnetization in the martensitic phase. This is the case for Ni–Mn–Ga alloys transforming martensitically well below the Curie point. In the following, we will show how the coupling of magnetism and structure affects the martensitic transition in magnetic shape memory alloys and will discuss the different magneto-mechanical and magneto-thermal properties derived from the coupling at different length scales.

3. Magnetic properties across the martensitic transition

Fig. 1 shows examples of the magnetization curves as a function of magnetic field for stoichiometric and non-stoichiometric Ni–Mn–Ga and for Ni–Mn–Sn and Ni–Mn–In at selected temperatures spanning the range where the martensitic transition occurs. From these curves, it is possible to derive the temperature dependence of the magnetization across the martensitic transition for different applied magnetic fields illustrated in Fig. 2. On cooling, the $Ni_{54.7}Mn_{20.3}Ga_{25.0}$sample undergoes a transition from a paramagnetic cubic phase to a ferromagnetic martensitic phase, which results in a marked increase of the magnetization at the transition. For the stoichiometric

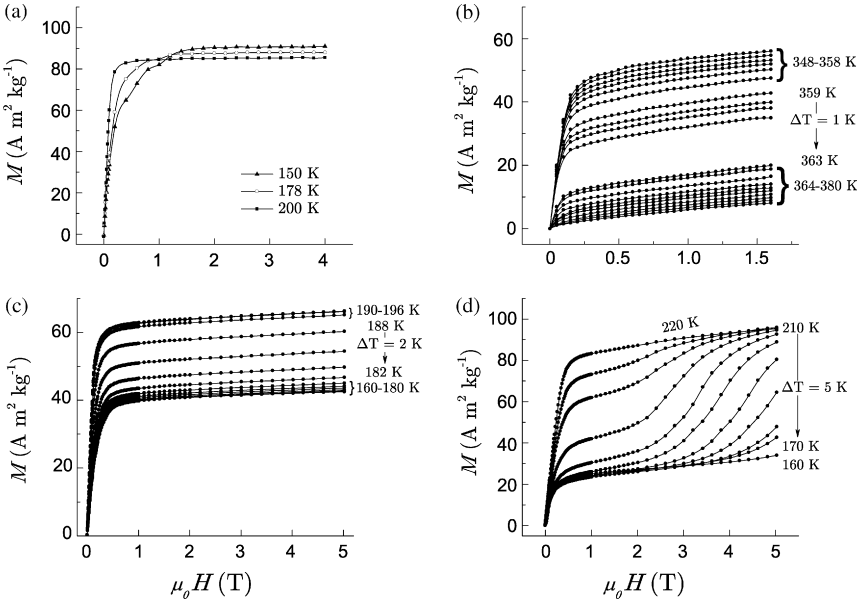

Fig. 1. Magnetization as a function of magnetic field at selected temperatures for: (a) $Ni_{49.5}Mn_{25.4}Ga_{25.1}$[3], (b) $Ni_{54.7}Mn_{20.3}Ga_{25.0}$[23], (c) $Ni_{50}Mn_{35}Sn_{15}$[16] and (d) $Ni_{50}Mn_{33.8}In_{15.9}$[17].