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Quantitative model of large magnetostrain effect in ferromagnetic shapell memory alloys

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Abstract. A quantitative model describing the large magnetostrain effect observed in several ferromagnetic shape memory alloys such as Ni_2MnGa is briefly reported.The paper contains an exact thermodynamic consideration of the mechanical and magnetic properties of similar types of materials. As a result, the basic mechanical state equation including magnetic field effect is directly derived from a general Maxwell relation. It is shown that the magnetic field induced deformation effect is directly connected with the strain dependence of magnetization. A simple model of magnetization and its dependence on the strain is considered and applied to explain the results of experimental study of large magnetostrain effects in Ni_2MnGa.

PACS. 75.80.+q Magnetomechanical and magnetoelectric effects, magnetostriction – 75.30.Gw Magnetic anisotropy

1 Introduction

In addition to some giant magnetostriction materials, ferromagnetic shape memory alloys were recently suggested as a general way for the development of a new class of the magnetic-field-controlled actuator materials [1–4,13,14]. It is now a goal of research projects in several groups directed at the development of ferromagnetic alloys exhibiting also a martensitic phase transition that would allow control of large strain effect by application of a magnetic field at constant temperature in a martensitic state. Numerous candidate shape memory materials were explored including Ni_2MnGa, Co_2MnGa, FePt CoNi, and FeNiCoTi during the past few years [5–7]. Magnetically driven strain effects are expected to occur in these systems. According to results reported in [8] the large strains of 0.19% can be achieved in a magnetic field of order 8 kOe in the tetragonal martensitic phase at 265 K of single-crystal samples of Ni_2MnGa. This strain is an order of magnitude greater than the magnetostriction effect of the parent, room temperature cubic phase.

Ni_2MnGa is an ordered L21 ferromagnetic Heusler alloy having at high temperature cubic ($a = 5.822$ Å) crystal structure that undergoes martensitic transformation at 276 K into a tetragonally distorted structure with crystalline lattice parameters: $a = b = 5.90$ Å and $c = 5.44$ Å [6]. The martensitic phase accommodates the lattice distortion connected with transformation by formation of three twin variants twinned usually on {110} planes and having the orientation of the tetragonal symmetry axes nearly parallel to three [100] directions. The saturation value of magnetization was found to be about 475 G. The magnetization curve of the low-temperature twinned phase usually displays a two-stage structure at 265 K [8] with a sharp crossover at about 1.7 kOe from easy low-field magnetization below to a hard stage above this value up to the 8 kOe saturation field value. Such a behaviour is assumed to be connected with a different response of different twin variants to the applied field. The measurements usually show a definite magnetostrain value along [100] as a function of the magnetic field applied in the same direction [8]. It is generally expected that a large macroscopic mechanical strain induced by the magnetic field in similar type systems is microscopically realized trough the twin boundaries motion and redistribution of different twin variants fractions in a magnetic field. The main thermodynamic driving forces have in this case a magnetic nature, connected with high magnetization anisotropy and differences in magnetization free energies for different twin variants of martensite [4,10,11].

The main goal of this brief publication is to give the right thermodynamic consideration of the mechanical and magnetic properties of similar types of materials and represent the quantitative model describing large magnetostrain effect observed in several ferroelastic shape memory alloys such as Ni_2MnGa. It is shown that the magnetic field induced deformation effect directly follows from the general thermodynamic rules such as Maxwell relations and connected with the strain dependence of

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magnetization. A simple model of magnetization for the internally twinned martensitic state and its dependence on the strain is considered and applied to explain the results of experimental studies of large magnetostrictive effects in Ni_2MnGa.

2 General thermodynamic consideration

Consider the general thermodynamic properties of the materials which can show both the ferroelastic and the ferromagnetic properties. Most of the shape memory alloys usually display ferroelastic behaviour in the martensitic state connected with redistribution of different twin variant fractions of martensite under the external applied stress through the motion of twin boundaries. Ferromagnetic shape memory materials have an additional possibility to activate the deformation process in a twinned martensitic state by the application of a magnetic field simultaneously with magnetization of the material. According to general thermodynamic principles both the mechanical and the magnetic properties of similar types of materials can be represented by the corresponding state equations:

$$\sigma = \sigma(\varepsilon, h) \tag{1}$$

$$m = m(\varepsilon, h) \tag{2}$$

where, equation (1) reflects the mechanical properties through stress-strain $\sigma - \varepsilon$ equation in the presence of a magnetic field h, and equation (2) gives the magnetization value m as a function of magnetic field applied h and strain ε. Both these equations can be obtained from an appropriate thermodynamic potential as follows:

$$\sigma(\varepsilon, h) = \frac{\partial}{\partial \varepsilon}\widetilde{G}(\varepsilon, h) \qquad m(\varepsilon, h) = -\frac{\partial}{\partial h}\widetilde{G}(\varepsilon, h) \tag{3}$$

where $\widetilde{G}(\varepsilon, h) = G(\varepsilon, h) - hm(\varepsilon, h)$, and $G(\varepsilon, h)$ is the specific Gibbs free energy at fixed temperature and pressure conditions. Both state equations are not completely independent functions and must satisfy known Maxwell's rule:

$$\frac{\partial}{\partial h}\sigma(\varepsilon, h) = -\frac{\partial}{\partial \varepsilon}m(\varepsilon, h). \tag{4}$$

Integration of this equation over the magnetic field starting from $h = 0$ at a fixed strain gives an important representation of the mechanical state equation including magnetic field effects:

$$\sigma = \sigma_0(\varepsilon) - \frac{\partial}{\partial \varepsilon}\int_0^h \mathrm{d}hm(\varepsilon, h). \tag{5}$$

According to this equation the external stress on the left is balanced in equilibrium by both the pure mechanical stress $\sigma_0(\varepsilon) = \sigma(\varepsilon, 0)$ resulting from the mechanical deformation of the material at $h = 0$ and the additional magnetic field induced stress that is represented by the second term on the right in this equation. It is also important to note that all the effect of the magnetic field on the mechanical properties is directly determined by the strain dependence of magnetization. In a particularly important case: $\sigma = \text{const.} = 0$ one can obtain a general equation determining magnetically induced strain (usually called a magnetic shape memory or MSM-effect) as follows:

$$\sigma_0(\varepsilon) = \frac{\partial}{\partial \varepsilon}\int_0^h \mathrm{d}hm(\varepsilon, h) \tag{6}$$

and its linearized solution:

$$\varepsilon^{\mathrm{msm}}(h) = \left(\frac{\mathrm{d}\sigma_0}{\mathrm{d}\varepsilon}\right)^{-1}_{\varepsilon=0}\left(\frac{\partial}{\partial \varepsilon}\int_0^h \mathrm{d}hm(\varepsilon, h)\right)_{\varepsilon=0} \tag{7}$$

that can be used when ε is much less than a martensite lattice tetragonal distortion value ε_0. Equation (7) follows from the lowest order Taylor's expansion on ε applied to equation (6) which is good at $\varepsilon \ll \varepsilon_0$, and usually observed experimentally. According to equations (6) and (7) the magnetization and its dependence on the strain is responsible for the MSM-effect and is the main subject for detailed discussion and modeling.

3 The model and its application to Ni_2MnGa tetragonal martensite

Consider a typical situation corresponding to measurements of large strain induced by the magnetic field in the tetragonal internally twinned martensite of Ni_2MnGa, obtained from the austenitic single crystal studied in [8], when the magnetic field is applied along [100] direction of parent austenitic phase and strain measurements were performed in the same axial direction. In this case the crystallographic [100] [010] [001] axes for each possible twin variant of the tetragonal martensitic phase will be nearly parallel to the external applied field. More exactly, additional small rotations of the tetragonal phase axes are expected but the corresponding rotation angles can not exceed a few degrees in the case of Ni_2MnGa and may be neglected for simplicity. Figure 1 schematically shows the expected alignment of the applied magnetic field, crystallographic orientations and magnetization curves for three possible tetragonal phase variants.

Therefore, the magnetic field is applied along the tetragonal symmetry axis only for one type of twin variant (which is called here the axial, or a-type) and simultaneously in the transversal direction in respect to the tetragonal symmetry axes of another two (transversal, or t-type) variants. The investigation of magnetization properties of Ni_2MnGa performed for a single tetragonal variant of martensite obtained by the mechanical compression method [12] has shown a considerable difference between the magnetization curves along the tetragonal [100] direction in comparison to another transversal [010] and [001] directions. It was found that a tetragonal axis

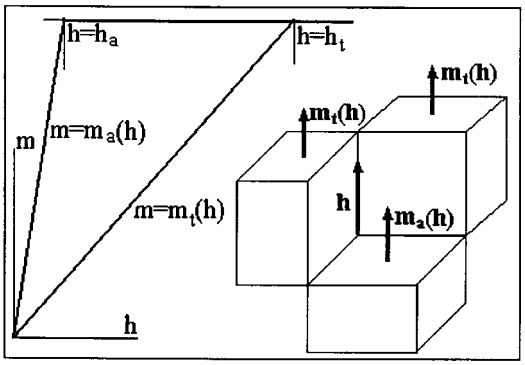

Fig. 1. Schematic representation of the magnetic field alignment and magnetization behaviour for three different crystallographic variants of the tetragonal martensitic phase.

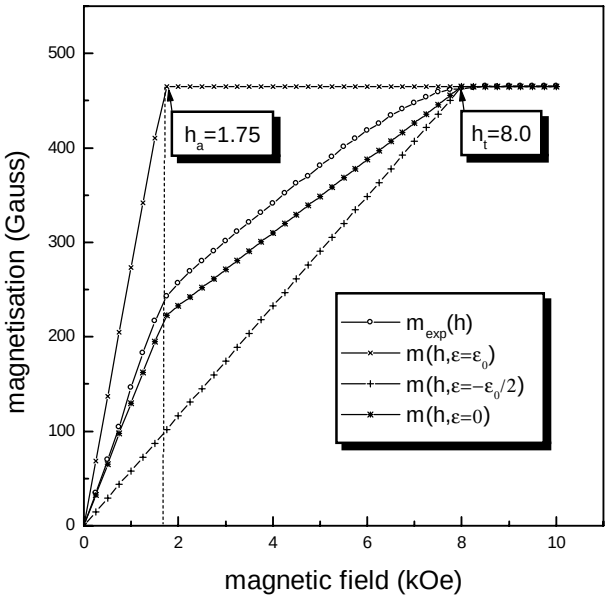

Fig. 2. Experimental and model magnetization curves along [001] direction that show the compression and tensile strain effect on the macroscopic magnetization of the martensitic phase caused by the relative change of the twin variant fractions.

is the easiest magnetization direction and requires considerably less value of saturation field $h_{\rm a}$ than a saturation field $h_{\rm t}$ characterizing magnetization in two hard transversal directions as it is schematically shown in Figure 1. In a general case the calculation of magnetization for the material with a complicated twin microstructure geometry requires a special approach. In this paper we will ignore, for simplicity, a similar type problem and will consider these effects in other publications. Taking into account the presence of magnetic anisotropy and difference in magnetization behaviour between the axial $m_{\rm a}(h)$ and transversal $m_{\rm t}(h)$ twin variants we consider a simple model of magnetization for the multi-variant martensitic state that gives the main contribution into magnetization insensitive to the fine details of twin microstructure. This model treats the multi-twin martensitic state as a composite material consisting of an easy magnetization area occupied by axial type twins and hard magnetization region of two transversal twin variants. Denoting as x the total volume fraction of the axial twin domain and $(1-x)$ - transversal type twin domain fractions, respectively, one can write the magnetization of the material as follows:

$$m\left(x,h\right)=xm_{\rm a}(h)+(1-x)m_{\rm t}(h) \tag{8}$$

where, $m_{\rm a}=(h)$ and $m_{\rm t}(h)$ are specific magnetization functions for the axial and transversal variants, respectively. On the other hand, the macroscopic strain along the axial direction can be found from a similar type of equation:

$$\varepsilon=x\varepsilon_{\rm a}^0+(1-x)\varepsilon_{\rm t}^0=\frac{3}{2}\varepsilon_0(x-\frac{1}{3}) \tag{9}$$

where the diagonal matrix elements $\varepsilon_{\rm a}^0=\varepsilon_0$ and $\varepsilon_{\rm t}^0=-\frac{1}{2}\varepsilon_0$ represent the relative tetragonal distortion of the martensite crystal lattice along its tetragonal axis and two transversal directions, respectively. A compression distortion $\varepsilon_0=5.4\%$ along the tetragonal symmetry axis was found in the case of Ni_2MnGa. One can easily eliminate the fractional dependence from these two equations and obtain the magnetization as a function of the macroscopic strain for the internally twinned martensitic state:

$$m\left(\varepsilon,h\right)=\left\{\frac{1}{3}m_{\rm a}(h)+\frac{2}{3}m_{\rm t}(h)\right\}+\frac{2}{3}\left(\varepsilon/\varepsilon_0\right)\left\{m_a(h)-m_t(h)\right\}. \tag{10}$$

This equation immediately reproduces all the main peculiarities of the experimental magnetization curve including the sharp change of its slope at $h=1.75$ kOe as indicated in Figure 2. This singularity appears exactly at $h=h_{\rm a}$ where the easy stage of magnetization process inside of the axial twin variants domain is finished. According to equation (10) $m\left(\varepsilon_0,h\right)=m_{\rm a}\left(h\right)$ and $m\left(-\varepsilon_0/2,h\right)=m_{\rm t}\left(h\right)$ so, one can use this fact to obtain both the $h_a=1.75$ kOe and $h=8$ kOe from the experimental magnetization curves measured in the multi-variant state. The model magnetization curve $m\left(0,h\right)$ corresponding to zero strain value shows the same type of behaviour and singularity in slope as the experimental one. The difference between them is caused by the second term in equation (10) that gives an additional strain dependent contribution into the magnetization. This contribution is directly connected with the MSM-effect and can be easily taken into account just after its calculation.

One can also obtain the final equations representing the effect of magnetic field on the strain by using basic expressions (7) derived before from the general thermodynamic consideration:

$$\varepsilon^{\rm msm}\left(h\right)=\frac{2}{3}\left(\varepsilon_0\frac{{\rm d}\sigma_0}{{\rm d}\varepsilon}\right)^{-1}_{\varepsilon=0}\int\limits_0^h{\rm d}h\left\{m_{\rm a}(h)-m_{\rm t}(h)\right\}. \tag{11}$$

4 Discussion and conclusions

As follows from this equation, two factors determine the strain value and its field dependence. The first one is proportional to the initial slope of stress-strain curve and can be found from the usual mechanical compression test without a magnetic field applied. The integral term reflects the effects of magnetic anisotropy and determines the functional magnetic field dependence of the strain. In particular, in the absence of magnetization anisotropy when $m_{\rm a}(h) = m_{\rm t}(h)$ the deformation effect also vanishes. The saturation level of the strain is achieved at $h = h_{\rm t}$ and above where $m_{\rm a}(h) = m_{\rm t}(h) = m^{\rm sat}$ and where the material has its maximal magnetization value $m^{\rm sat}$. One can easily obtain the corresponding saturation value of the strain performing the necessary integrations in equation (11) as follows:

$$\varepsilon_{\rm sat}^{\rm msm} = \frac{1}{3}\left(\varepsilon_0 \frac{{\rm d}\sigma_0}{d\varepsilon}\right)^{-1}_{\varepsilon=0} (h_{\rm t} - h_{\rm a})\, m^{\rm sat}. \qquad (12)$$

Precise quantitative estimation of the saturation strain requires, in general, the corresponding mechanical testing. Here, we will use a simple estimation of ${\rm d}\sigma_0/{\rm d}\varepsilon \sim \sigma_0/\varepsilon_0$. So, $\varepsilon_{\rm sat}^{\rm msm} \sim \frac{1}{3}(\sigma_0)^{-1}(h_{\rm t} - h_{\rm a})\, m^{\rm sat}$ where the characteristic stress σ_0 representing ferroelastic mechanical behavior of the material is expected to be about of 20 MPa in Ni_2MnGa martensite. Using also the values of $h_{\rm t} \sim 8$ kOe, $h_{\rm a} \sim 1.75$ kOe and $m^{\rm sat} \sim 475$ G found from the magnetization curve analysis one can obtain a simple estimation: $\varepsilon_{\rm sat}^{\rm msm} \sim 0.49\%$. The more precise estimation that follows from the mechanical testing results gives ${\rm d}\sigma_0/{\rm d}\varepsilon \sim (2 \div 3)\,\sigma_0/\varepsilon_0$. Consequently, $\varepsilon_{\rm sat}^{\rm msm} \sim (0.24 \div 0.16)\%$ which is in a better quantitative agreement with $\varepsilon_{\rm sat}^{\rm msm} \sim 0.14\%$ experimental value. In order to achieve the larger magnetostrain effect comparable with the lattice tetragonal distortion value $\varepsilon_0 \sim 5\%$ one will need materials with a very low $\sigma_0 \sim 2$ MPa detwinning stress value. This task can be considered as the realistic one because the observation of $\sigma_0 \sim 2$ MPa [6] was reported in some publications.

Figure 3 shows the field behavior of the strain that follows from the model and its change for the different values of the magnetic anisotropy factor $k = h_{\rm a}/h_{\rm t}$ defined as a ratio between the axial and transversal saturation fields.

The dimensionless strain response $\varepsilon^{\rm msm}(h)/\varepsilon_{\rm max}$ normalized by,

$$\varepsilon_{\rm max} = \frac{1}{3}\left(\varepsilon_0 \frac{{\rm d}\sigma_0}{{\rm d}\varepsilon}\right)^{-1}_{\varepsilon=0} h_{\rm t} m^{\rm sat} \qquad (13)$$

increases from zero value at $k = 1$ simultaneously with a corresponding shape change and shows the maximal possible deformation effect and linear type singularity for the low field strain behavior at $k = 0$. This case corresponds to the maximally strong anisotropy when the axial saturation field becomes infinitely small $h_{\rm a} \longrightarrow 0$ and $m_{\rm a}(h)$ immediately achieves its saturation level $m^{\rm sat}$ starting from an arbitrary low magnetic field and then still remains equal to a constant $m^{\rm sat}$ value during the magnetization process. Therefore, one can conclude that a linear low field behavior usually predicted in some previously developed models [10,11] is directly connected with their assumption on the complete saturation of magnetization for the axial type twin variants. According to the present model such a type of assumption can be physically reasonable in the limit $h_{\rm a} \longrightarrow 0$ only. In other case the strain shows the normal parabolic type behavior in the low field $h < h_{\rm a}$ region in agreement with the experimental observations. A good correspondence between the model and experimental results is indicated in Figure 4. We neglected here the small hysteresis effects which are usually observed assuming to give later the more detailed discussion of this problem by using some new developments and quantitative descriptions of hysteresis in shape memory materials.

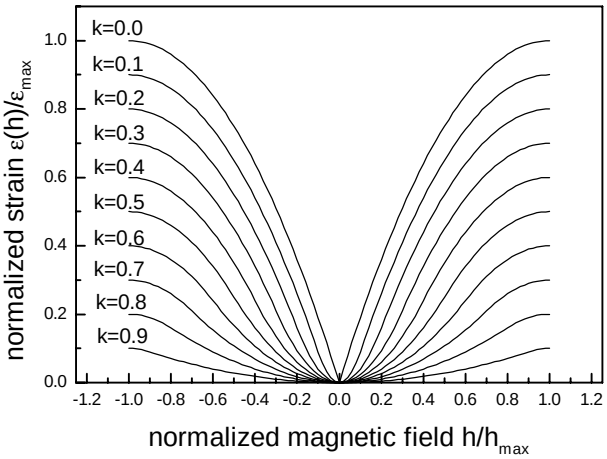

Fig. 3. Magnetic anisotropy effect on the strain *vs.* magnetic field behavior according to the model calculations.

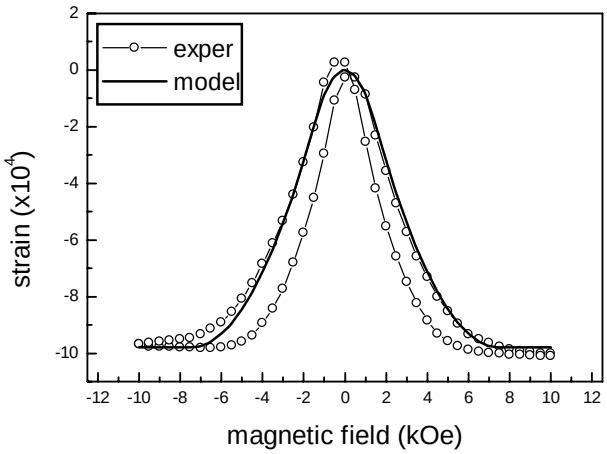

Fig. 4. Magnetostrain effect: comparison of results between the model and the experiment

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