QUANTITATIVE MODEL OF LARGE MAGNETOSTRAIN EFFECT IN FERROMAGNETIC SHAPE MEMORY ALLOYS

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A quantitative model describing large magnetostrain effect observed in several ferromagnetic shape memory alloys such as Ni$_2$MnGa is briefly reported. The paper contains an exact thermodynamic consideration of the mechanical and magnetic properties of a similar type materials. As a result, the basic mechanical state equation including magnetic field effect is directly derived from a general Poisson’s rule. It is shown that the magnetic field induced deformation effect is directly connected with the strain dependence of magnetisation. A simple model of magnetisation and its dependence on the strain is considered and applied to explain the results of experimental study of large magnetostrain effects in Ni$_2$MnGa.

I. INTRODUCTION

In addition to some giant magnetostriction materials, ferromagnetic shape memory alloys was recently suggested as a general way for the development of a new class of the magnetic-field-controlled actuator materials [1,2,3,4,13,14]. It is now a goal of research projects in several groups directed on 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$_2$MnGa, Co$_2$MnGa, FePt CoNi, and FeNiCoTi during past few years [5,6,7]. Magnetically driven strain effect is 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$_2$MnGa. This strain is an order of magnitude greater than the magnetostriction effect of the parent, room temperature cubic phase.

Ni$_2$MnGa is an ordered by 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 [9]. 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 to three possible [100] directions. The saturation value of magnetization was found to be about of 475 G. Magnetization curve of the low-temperature twinned phase usually displays two-stage structure at 265 K [9] with a sharp crossover at about of 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 behavior is 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 [9]. It is generally expected that a large macroscopic mechanical strain induced by the magnetic field in similar type systems is microscopically realized through the twin boundaries motion and redistribution of different twin variants fractions in a magnetic field. The main thermodynamic driving forces have in this case magnetic nature and connected with high magnetization anisotropy and differences in magnetization free energies for different twin variants of martensite [9,10,11].

The main goal of this brief publication is to give the right thermodynamic consideration of the mechanical and magnetic properties of a similar type materials and represent the quantitative model describing large magnetostrain effect observed in several ferroelastic shape memory alloys such as Ni$_2$MnGa. It is shown that the magnetic field induced deformation effect directly follows from the general thermodynamic rules such as Poisson equation and connected with the strain dependence of magnetization. A simple model of magnetisation for the internally twinned martensitic state and its dependence on the strain is considered and applied to explain the results of experimental study of large magnetostrictive effects in Ni$_2$MnGa.
II. 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 behavior in martensitic state connected with redistribution of different twin variant fractions of martensite under the external stress applied 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 magnetic field simultaneously with magnetization of the material. According to general thermodynamic principles both the mechanical and the magnetic properties of similar type materials can be represented by the corresponding state equations:

\[ \sigma = \sigma(\varepsilon, h) \] (1)

\[ m = m(\varepsilon, h) \] (2)

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

\[ \sigma(\varepsilon, h) = \frac{\partial}{\partial \varepsilon} \tilde{G}(\varepsilon, h) \]

\[ m(\varepsilon, h) = -\frac{\partial}{\partial h} \tilde{G}(\varepsilon, h) \] (3)

where, \( \tilde{G}(\varepsilon, h) = G(\varepsilon, h) - hm(\varepsilon, h) \), and \( G(\varepsilon, h) \) is the specific Gibbs free energy at fixed temperature and pressure condition. Both state equation are not completely independent functions and must satisfy known Poisson’s rule:

\[ \frac{\partial}{\partial h} \sigma(\varepsilon, h) = -\frac{\partial}{\partial \varepsilon} m(\varepsilon, h) \] (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:

\[ \sigma = \sigma_0(\varepsilon) - \frac{\partial}{\partial \varepsilon} \int_0^h dhm(\varepsilon, h) \] (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: \( \sigma = const = 0 \) one can obtain a general equation determining magnetically induced strain (usually called as a magnetic shape memory or MSM-effect) as follows:

\[ \sigma_0(\varepsilon) = \frac{\partial}{\partial \varepsilon} \int_0^h dhm(\varepsilon, h) \] (6)

and its linearized solution:

\[ \varepsilon^{msm}(h) = \left( \frac{d\sigma_0}{d\varepsilon} \right)^{-1}_0 \int_0^h \left( \frac{\partial}{\partial \varepsilon} \int_0^h dhm(\varepsilon, h) \right)_\varepsilon=0 \] (7)

that can be used when \( \varepsilon \) is much less than a martensite lattice tetragonal distortion value \( \varepsilon_0 \). According to Eqns. (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.
Consider a typical situation corresponding to measurements of large strain induced by the magnetic field in the tetragonal internally twinned martensite of Ni$_2$MnGa 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 all three possible twin variants of the tetragonal martensitic phase will be nearly parallel to the external field applied. More exactly, the crystallographic orientation relationships between the austenitic and martensitic phases can be obtained by using the usual methods of the crystallographic theory. Additional small rotations of the tetragonal phase axes are expected but the corresponding rotation angles can not exceed few degrees in the case of Ni$_2$MnGa and may be neglected for simplicity.

Fig.1. schematically shows the expected alignment of the magnetic field applied, crystallographic orientations and magnetization curves for three possible tetragonal phase variants.

\[ m(x, h) = x m_a(h) + (1 - x) m_t(h) \]  \hspace{1cm} (8)

where, \( m_a(h) \) and \( m_t(h) \) 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 equation:

\[ \varepsilon = x \varepsilon_a^0 + (1 - x) \varepsilon_t^0 = \frac{3}{2} \varepsilon_0(x - \frac{1}{3}) \]  \hspace{1cm} (9)

where, the diagonal matrix elements \( \varepsilon_a^0 = \varepsilon_0 \) and \( \varepsilon_t^0 = -\frac{1}{2} \varepsilon_0 \) represent the relative tetragonal distortion of the martensite crystal lattice along its tetragonal axis and two transversal directions, respectively. The compression distortion \( \varepsilon_0 = 5.4\% \) along the tetragonal symmetry axis was found in case of Ni$_2$MnGa. One can easily exclude the fraction dependence from these two equations and obtain the magnetization as function of the macroscopic strain for the internally twinned martensitic state:

\[ m(\varepsilon, h) = \left\{ \frac{1}{3} m_a(h) + \frac{2}{3} m_t(h) \right\} + \frac{2}{3} (\varepsilon/\varepsilon_0) \{ m_a(h) - m_t(h) \} \]  \hspace{1cm} (10)

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

\[
\varepsilon_{\text{sat}} = \frac{1}{3} \left( \varepsilon_0 \frac{d\sigma_0}{d\varepsilon} \right)^{-1} \int_{\varepsilon=0}^{h} dh \{ m_a(h) - m_t(h) \}
\]  

(11)

IV. 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 slope of stress-strain curve and can be found from the usual mechanical compression test without 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 absence of the magnetization anisotropy when \( m_a(h) = m_t(h) \) deformation effect is also vanishes. The saturation level of the strain is achieved at \( h = h_t \) and above where \( m_a(h) = m_t(h) = m_{\text{sat}} \) and where the material has its maximal magnetization value \( m_{\text{sat}} \). One can easily obtain the corresponding saturation value of the strain performing the necessary integrations in Eq.(11) as follows:

\[
\varepsilon_{\text{sat}} = \frac{1}{3} \left( \varepsilon_0 \frac{d\sigma_0}{d\varepsilon} \right)^{-1} (h_t - h_a) m_{\text{sat}}
\]  

(12)

Precise quantitative estimation of the saturation strain requires, in general, the corresponding mechanical testing. Here, we will use a simple estimation of \( d\sigma_0/d\varepsilon \sim \sigma_0/\varepsilon_0 \). So, \( \varepsilon_{\text{sat}} \sim \frac{1}{3} (\sigma_0)^{-1} (h_t - h_a) m_{\text{sat}} \) where the characteristic stress \( \sigma_0 \) representing ferroelastic mechanical behavior of the material is expected to be about of 20MPa in Ni$_2$MnGa martensite. Using also the values of \( h_t \sim 8kOe \), \( h_a \sim 1.75kOe \) and \( m_{\text{sat}} \sim 475G \) found from the magnetization curve analysis one can obtain a simple estimation: \( \varepsilon_{\text{sat}} \sim 0.49\% \). More precise estimation that follows from the mechanical testing results gives \( d\sigma_0/d\varepsilon \sim (2 \div 3) \sigma_0/\varepsilon_0 \). Consequently, \( \varepsilon_{\text{sat}} \sim (0.24 \div 0.16)\% \) which is in a better quantitative agreement with \( \varepsilon_{\text{sat}} \sim 0.14\% \) 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 very low \( \sigma_0 \sim 2MPa \) detwinning stress value. This task seems can be considered as the realistic one because the observation of \( \sigma_0 \sim 2MPa \) and \( \sigma_0 \sim 8MPa \) were reported in some publications.

Fig.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 \( k = h_a/h_t \) defined as a ratio between the axial and transversal saturation fields.

\[
\varepsilon_{\text{sat}}^{\text{ MSM}}(h) = \frac{2}{3} \left( \varepsilon_0 \frac{d\sigma_0}{d\varepsilon} \right)^{-1} \int_{\varepsilon=0}^{h} dh \{ m_a(h) - m_t(h) \}
\]  

(13)

The dimensionless strain response \( \varepsilon_{\text{sat}}^{\text{ MSM}}(h)/\varepsilon_{\text{max}} \) normalized by,
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 $h_a \to 0$ only. In other case the strain shows the normal parabolic type behavior in the low field $h < h_a$ region in agreement with the experimental observations. A good correspondence between the model and experimental results is indicated in Fig. 4. We neglected here the small hysteresis effects which are usually observed assuming to give the more detailed discussion of this problem by using some new developments and quantitative descriptions of hysteresis in shape memory materials.

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

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\[ m_{\text{exp}}(h) \]
\[ m(h, \epsilon = \epsilon_0) \]
\[ m(h, \epsilon = -\epsilon_0/2) \]
\[ m(h, \epsilon = 0) \]
