Mechanomagnetic spectroscopy of ferromagnetic shape memory alloys

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We have used a recently designed mechanomagnetic spectroscopy technique to study the inverse magnetoelastic effect (stress-induced magnetization) in ferromagnetic materials simultaneously with their elastic and anelastic properties. Special attention has been paid to ferromagnetic shape memory alloys. Application of mechanomagnetic spectroscopy technique allows one to study the stress-induced motion of elastic (by means of the anelasticity measurements) and magnetic domain boundaries (through the detection of the stress-induced magnetization). The experimental technique is based on the piezoelectric ultrasonic composite oscillator technique with an additional magnetic channel, enabling to register the induction, produced by the strain of a ferromagnetic sample, down to 10⁻¹⁰ T. Examples of application of this new technique are given, which include observation of a temperature–magnetic field domain wherein magnetoelastic coupling demonstrates variations of sign and analysis of magnetic domain wall dynamics in polycrystalline ferromagnetic martensites.

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1. Introduction

Mechanical stress substantially affects magnetic properties of most ferromagnetic materials. Following Bozorth [1], mechanical stress should be ranked together with field and temperature among the parameters of primary importance. Magnetoelastic interactions in traditional ferromagnetic materials are behind this coupling of mechanical and magnetic properties. The most direct manifestations of the magnetoelastic coupling are the well-known direct and inverse magnetostriction effects. In ferromagnetic martensites, which are characterized by coexistence of two interacting subsystems of elastic and magnetic domains, application of magnetic field can induce giant magnetic field induced strains up to 10% [2,3], which allowed calling them ferromagnetic shape memory alloys (FSMA). Coupling between elastic and magnetic domain subsystems, substantiated now by the magnetocrystalline anisotropy, is behind magnetic field induced strains. Traditional spectroscopy techniques permit only separate studies of mechanical (e.g. elastic and anelastic) and magnetic (e.g. susceptibility, magnetization) properties of ferromagnetic materials in general and in FSMA in particular. As a rule, the role of the conjugate (mechanical/magnetic) subsystem remains only minor in magnetic/mechanical spectroscopy experiments. Probably the only exception in mechanical spectroscopy experiments is the magnetoelastic damping which can be predominant in conventional ferromagnetic alloys. Data on anelasticity of FSMA are scarce [4–6] and the present authors are not aware of any study of magneto-mechanical damping in FSMA, where the contribution of the mechanical subsystem of elastic domains might be the major part of damping. Preliminary studies of the hysteretic magnetomechanical damping in FSMA show that its role is only minor at least in polycrystalline alloys [7]. Therefore, the possibility to characterize the magnetic subsystem in FSMA through mechanical spectroscopy experiments is likely lost.

Below we give the description of a recently designed technique [8] for the detailed investigation of both mechanical and magnetic responses of ferromagnets to applied oscillatory stress, enabling thus direct investigations of magnetoelastic coupling in ferromagnets under periodic excitation. The experimental technique is based on the piezoelectric composite oscillator technique (PUCOT) [9,10], combined with the measurements of the inverse magnetostriction effect, also known as Villari effect.

In this paper we give examples of application of the above-mentioned technique, which has been referred to as mechanomagnetic spectroscopy [8].

2. Experimental studies of the inverse magnetostriction

The method used can be illustrated assuming for simplicity an isotropic ferromagnetic material with saturation magnetostriction $\lambda_s$. An applied mechanical stress $\sigma$ induces a magnetoelastic energy per unit volume

$$W_{me} = \frac{3}{2} \lambda_s \sigma \sin^2 \theta,$$

(1)
where $\theta$ is the angle between the magnetization and stress directions. Eq. (1) describes the uniaxial anisotropy produced by mechanical stress with anisotropy axis along the stress direction, which is of an easy axis type for $\lambda_\sigma > 0$ and of an easy plane type if $\lambda_\sigma < 0$. Thus, because of the magnetoeelastic energy involved, applied stress acts on non-180° domain walls as an effective anisotropy field $H_\sigma$:

$$H_\sigma \equiv \frac{3}{2} \frac{\lambda_\sigma}{\mu_0 M_s} \sigma,$$

where $M_s$ is the saturation magnetization.

Application of a cyclic stress (under fixed applied field), thus, will lead to a periodic variation of the magnetization of the sample (partially magnetized), or the inverse magnetostriiction or Villari effect. Periodic magnetization variations produced by oscillatory stress can be registered by means of a pickup coil placed around the sample under stress. Until now, the Villari effect under cyclic mechanical excitation has been studied using low-frequency loadings (∼10 Hz) in a testing machine [11], resonant oscillations of rods induced by magnetostrictive transducers [12,13] or piezoelements [14] (frequency ∼10^4 Hz) as well as for propagating ultrasonic pulses (frequency ∼400 kHz) [14]. Investigations of the inverse magnetostriiction effect have so far been performed at ambient temperatures as a function of stress amplitude and applied polarizing field in classical materials like Fe, Ni, industrial steels and permalloy. The restriction of these techniques to ambient temperatures is an apparent drawback, especially as far as ferromagnetic martensites are concerned, in which both the para-ferromagnetic and the martensitic transformation could not be assessed.

Recently, combining high precision PUCOT technique operating at a frequency of around 100 kHz [10] with magnetic measurements has been suggested [8], enabling this way parallel investigations of elastic, anelastic properties and magnetoelectric coupling in ferromagnets. Fig. 1 shows a schematic drawing of the composite oscillator and magnetic pickup system. The four component oscillator consists of quartz transducers (drive and gauge ones), a ferromagnetic sample and intermediate rod of low-damping non-magnetic Al–Mg alloy, which spatially separates piezoelectric quartz transducers from the pickup coil. The latter is placed around the stress anti-node position in the middle part of the half-wave long ferromagnetic sample. The stress-induced induction of the sample is obtained from the changes of the flux $\Phi$ penetrating the pickup coil. The amplitude of the first harmonic of voltage $V_0$ induced in the pickup coil is

$$V_0 = -n \left( \frac{d\Phi}{dt} \right)_{\text{max}} = -nS\omega B_0,$$

where $n$ and $S$ are the number of turns and the area of the pickup coil, $\omega$ is the angular frequency and $B_0$ is the amplitude of the first harmonic of stress-induced variations of induction. If the return flux in between the sample and small coil is neglected, $S$ becomes the cross-section of the sample and Eq. (3) gives the stress-induced variations of the induction in the sample. Proper screening, cable connecting and using a lock-in amplifier allow one to obtain the background signal (in the absence of oscillating ferromagnetic sample) as low as around 10^{-10} T. The magnetic measuring channel (registering the phase and the magnitude of the stress-induced induction) is added to the PUCOT equipment, which allows a wide variety of experiments in the temperature–strain amplitude domain, see e.g. examples in Refs. [10,15]. This way, the equipment permits mechanomagnetic spectroscopy studies to be performed over temperatures (80–370 K) over wide range of strain amplitudes (10^{-7} to 10^{-4}) and under axial fixed or cyclic polarizing field up to 12 kA/m.

The examples will be given below of application of the mechanomagnetic spectroscopy technique to study peculiarities of magnetoelectric coupling and the dynamics of magnetic domain boundaries under oscillatory stress in polycrystalline ferromagnetic martensites.

3. Peculiarities of magnetoelectric coupling in ferromagnetic martensites

This section will deal with the results obtained for a polycrystalline Ni_{53.5–Fe_{6.5–Ga_{27–Co_{0}}} FSMA. For this composition, the martensitic phase of the alloy contains a mixture of non-layered (2M) and 7-layered (14M) structures, with tetragonal and orthorhombic unit cells, respectively [16]. Data will be shown for samples quenched (WQ) or air cooled (AC) after annealing for 900 s at a temperature of 970 K. These heat treatments correspond to low and high degrees of long-range L2₁ atomic order, respectively. For the present alloy, martensite is strongly stabilized in quenched samples; the first reverse transformation temperature is shifted to around 580 K [16]. Air-cooled samples are not prone to the stabilization and demonstrate a nominal start reverse transformation temperature $T_r$ around 365 K. Quenching also affects strongly the para-ferromagnetic transition: the Curie temperature $T_C$ was found to be around 320 K for the air-cooled sample whereas after water quenching the transition became very diffuse [17] and the $T_C$ was shifted to a temperature of around 280 K.

Temperature spectra of the magnitude (modulus) and phase of the stress-induced induction are depicted in Fig. 2 for air-cooled (a) and quenched samples (b). During spectra measurements the axial polarizing field was kept constant at 4.6 kA/m. Data shown in Fig. 2 were measured for an oscillatory strain amplitude of $2 \times 10^{-5}$. The most prominent observation is the existence, for each sample, of two deep minima of the magnetic induction concurrent with a rapid variation of phase by nearly 180°. The high-temperature minimum of induction is very close to (somewhat below) the Curie temperature, whereas the low-temperature one occurs in the ferromagnetic state of the samples. The significance of the variation of phase of the induction is clarified considering stress-induced
induction under periodic axial field. Fig. 3(a) shows the magnitude and phase of the stress-induced induction, for the same air-cooled sample as in Fig. 2(a), under the effect of cyclic polarizing field applied at 290 K. During cycling the field, the oscillatory strain amplitude was again kept fixed at a value of $2 \times 10^{-5}$, corresponding to a stress amplitude of 1.47 MPa for the Young’s modulus value of 73.5 GPa. The induction demonstrates two deep minima after each change of the sign of applied field. The phase changes in a step-like manner by 180° just at the position of these minima, similar to the results in Fig. 2. The strong effect observed in the magnetic response is in dramatic contrast with apparent insensitivity of the anelasticity to the polarizing field: Fig. 3(b) indicates that relative variations of the decrement are comparable with the scatter of experimental points and do not exceed $3 \times 10^{-3}$. These variations are monotonous and in fact reflect time-dependence of damping in martensite due to mobility of pinning points. Insensitivity of damping to applied field, in agreement with Ref. [7], points to a minor contribution of magnetomechanical damping to the total anelasticity of polycrystalline ferromagnetic martensites. Fig. 3(c) shows the in-phase and in-quadrature components of the induction signal calculated from the modulus and phase data. It should be emphasized here that so far we are not able to determine the true sign of the inverse magnetostriiction effect, since we do not distinguish compressive and tensile stresses in the sample. That means that the induction is determined except for the sign (in other words, the phase is determined with possible shift of 180°).

The above analysis of the hysteresis loops indicates that the rapid changes of the phase in temperature spectra (Fig. 2) together with minima in induction signal also correspond to the change of the sign of the stress-induced induction. Temperature spectra of in-phase components of the stress-induced induction for WQ and AC samples are plotted in Fig. 4(a). The induction changes its sign twice: first just above the $T_c$ temperature and also at lower temperatures in the ferromagnetic state of the martensite. Since these changes of polarity correspond to fixed applied field and nearly constant oscillatory stress (the elastic strain amplitude is fixed under the present experimental conditions), these variations of the sign of induction point to the change of the sign of magnetostriiction.

The existence of points along the magnetization curves, where the induction loses its sensitivity to applied stress and the effect of stress inverts its sign, or where $(\partial B/\partial \sigma)_H = 0$, is known since the middle of the XIX century. Such points along the magnetization curves have been historically called Villari critical points [18] or Vill-
Fig. 4. Temperature spectra of the in-phase component of stress-induced induction (a) for quenched (WQ) and air-cooled (AC) samples of a Ni$_{53.5}$–Fe$_{16.5}$–Ga$_{27}$–Co$_3$ alloy, registered for constant strain amplitude of $2 \times 10^{-5}$ under polarizing axial field of 4.6 kA/m. In (b) the temperature spectra of the decrement $\delta$ for two values of strain amplitude ($2 \times 10^{-5}$ and $10^{-6}$) are shown together with their difference, $\delta_h$. Damping data were obtained during the same temperature scan as the stress-induced induction in (a).

Villari reversals [1]. Application of the mechanomagnetic spectroscopy has shown that for certain temperatures (applied magnetic fields) cyclic stress does not produce variations of magnetization. Thus, our data point to the existence of Villari critical points (or differential Villari critical points, since we deal with rather small periodic and not quasistatic stress) over certain temperature domain.

Temperature spectra of damping in the WQ sample for strain amplitudes of $10^{-6}$ and $2 \times 10^{-5}$ and of the strain-amplitude-dependent decrement as a difference between the high- and low-amplitude values, Fig. 4(b), were obtained simultaneously with the stress-induced induction depicted in Fig. 4(a). Apparently, the anelasticity for a WQ sample again demonstrates only marginal variations at the temperatures of Villari critical points.

The behaviour of the stress-induced magnetization under cyclic polarizing field at several temperatures in the vicinity of Villari critical points for a WQ sample is depicted in Fig. 5. The results were obtained for increasing temperatures starting from 210 K. Experimental data demonstrate a dramatic variation close to the critical points. The loops remind closely the acoustic “signatures” obtained by the acoustic coupling technique [19] and can be considered as magnetic “signatures” of magnetoelastic coupling effect. The induction in each loop reaches nearly zero value twice: each time close to the coercive field. The existence of the Villari critical point is characterized by the appearance of a new zero (or minimum) of induction at a corresponding value of polarizing field, see the loops for 240 and 283 K, Fig. 5(a) and (c). These changes of sign of the stress-induced magnetization are detected if the account is taken for the phase variation along magnetic cycles, plotting the corresponding stress-induced induction—applied field loops, Fig. 6. According to Fig. 6(a), approaching the critical point at around 240 K, a minimum for positive $H$ (and a maximum for negative $H$) appears for low values of applied field, which deepens and extends towards higher $H$ values so as to displace the loop from the I and the III quadrants into the II and IV. Interestingly, the coercive field remains very low over this temperature range. On further temperature increase from 260 K, the minimum (maximum) at around 4 kA/m gradually disappears, Fig. 6(b), and the loops are displaced back into the I and the III quadrants, Fig. 6(c). This time, such transformation is accompanied by a dramatic variation of the coercive force, which points to a substantial rearrangement of magnetic domain structure close to $T_c$. Data of Fig. 6 lead to the very important conclusion that Villari critical points exist only for low values of applied field. Indeed, extrapolation of all loops to somewhat higher values of external field is expected to yield in all cases the loops positioned within the I and the III quadrants.

Feasible mechanisms for the formation of critical points in the temperature domain have been discussed in Ref. [20]. First of all, the high-temperature Villari critical point is by all means related to variations of magnetoelastic coupling constants during formation of magnetic domain structure close to the critical temperature of para-ferromagnetic transition. Interestingly, magnetic susceptibility is insensitive to this effect and demonstrates a monotonous increase of permeability on approaching the $T_c$ temperature. We believe that the measurements of magnetostriiction are also unable to detect this change of the sign of magnetoelastic coupling close to the $T_c$ temperature: the magnetostriction takes very low val-
Moreover, within this scenario it is difficult to explain the restriction amplitude of temperatures. Data for a frequency of polarizing field of 0.002 Hz and oscillatory stress amplitudes close to the Curie temperature, near 307 and 275 K, respectively. Martensitic phase demonstrated mostly the 6-layered stacking sequence. Variations of the magnitude of stress-induced induction as a function of oscillatory stress amplitude are shown in Fig. 7 for the austenitic (a) and martensitic (b) states of the material. A small magnetic signal was always detected in the thermally demagnetized state of the sample and should be attributed to some residual magnetization of the sample. The stress-induced induction rises rapidly with polarizing field, both in the austenitic (Fig. 7(a)) and in the martensitic states (Fig. 7(b)), the stress-induced induction of the martensite being 3–4 times lower than that of the austenite for the same values of external field. The stress amplitude dependence of induction fit straight lines on the logarithmic scale in Fig. 7 both in the martensitic and in the austenitic states.

4. Dynamics of magnetic domain boundaries in polycrystalline FSMA

As previously mentioned, FSMA, apart from conventional magnetostriction, can present giant magnetic field induced strains due to the coherent motion of the magnetic and elastic domain boundaries in alloys with high values of magnetocrystalline anisotropy [2,3]. During quasistatic deformation, the macroscopic induction change of a single crystalline Ni–Mn–Ga polyvariant sample was found to be proportional to its macroscopic strain due to such coherent motion of elastic and magnetic domain boundaries [32]. The existence of coupling between the motion of elastic and magnetic domains in a polycrystalline Ni$_{53.5}$–Fe$_{16.5}$–Ga$_{27}$ alloy in a range of small oscillatory displacements of elastic twins and low values of reversible stress-induced induction (between $10^{-9}$ and $10^{-5}$ T) has been checked using mechanomagnetic spectroscopy [8]. Some important conclusions concerning the dynamics of magnetic domain boundaries have also been drawn in Ref. [8].

A ternary Ni$_{54}$–Fe$_{19}$–Ga$_{27}$ FSMA had been studied in the highly ordered state, obtained by air cooling the samples after annealing for 900 s at 1120 K. The Curie and the start of the direct martensitic transformation temperatures were around 307 and 275 K, respectively. Martensitic phase demonstrated mostly the 6-layered stacking sequence. Variations of the magnitude of stress-induced induction as a function of oscillatory stress amplitude are shown in Fig. 7 for the austenitic (a) and martensitic (b) states of the material. A small magnetic signal was always detected in the thermally demagnetized state of the sample and should be attributed to some residual magnetization of the sample. The stress-induced induction rises rapidly with polarizing field, both in the austenitic (Fig. 7(a)) and in the martensitic states (Fig. 7(b)), the stress-induced induction of the martensite being 3–4 times lower than that of the austenite for the same values of external field. The stress amplitude dependences of induction fit straight lines on the logarithmic scale in Fig. 7 both in the martensitic and in the austenitic states

$$B_0 \propto \sigma_0^p.$$  (4)
Fittings of the curves for an external field of 3.0 kA/m by exponents (4) are shown in Fig. 7 indicating essentially linear dependences. Fig. 8(a) demonstrates the stress amplitude dependence of the total logarithmic decrement in the austenitic and martensitic states during the same stress amplitude scans as for the data in Fig. 7. The stress-amplitude-dependent part of the decrement and Young’s modulus defect is represented in Fig. 8(b). The non-linear (stress amplitude dependent) anelasticity, i.e. both the stress amplitude dependent decrement $\delta_h$ and the Young’s modulus defect $(\Delta E/E)_h$, over a wide range of low and moderate stress amplitudes also conforms with a power law: a straight line in Fig. 8(b) shows the fitting of the amplitude-dependent decrement in the martensitic state with a power law

$$\delta_h \propto (\Delta E/E)_h \propto \sigma_0^n$$

(5)

with the stress exponent close to 3/2: $n = 1.43$.

If Eq. (5) holds, the anelastic strain is also a power function of stress amplitude

$$\varepsilon_0^m \propto \sigma_0^m$$

(6)

with an exponent $m = n + 1$ or approximately 5/2.

Thus, the stress-induced induction of the sample is essentially a linear function of the stress amplitude, whereas the anelastic strain is essentially non-linear. This property seems to be peculiar in polycrystalline ferromagnetic martensites. Results of control experiments, performed for a well-annealed (7 h at 1170 K) polycrystalline Fe (purity of 99.99%) are presented in Fig. 9. Fig. 9 shows the stress-induced induction normalized by the value of stress amplitude $\sigma_0$, which becomes substantially non-linear for strain

$$B_0/\sigma_0$$

Fig. 8. Stress amplitude dependence of the total decrement $\delta$ (a), and of the non-linear components of decrement $\delta_h$ and modulus defect $(\Delta E/E)_h$ (b), registered in the martensitic ($T = 259$ K) and austenitic ($T = 287$ K) states of an air-cooled sample of Ni$_{54}$Fe$_{19}$Ga$_{27}$ alloy. Data for the austenitic state are given for demagnetized state and under axial polarizing field of 3.0 kA/m.

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Fig. 9. Strain amplitude dependence of the decrement $\delta$ and normalized magnitude of stress-induced induction $B_0/\sigma_0$ for an annealed sample of pure iron.
amplitudes beyond approximately $2 \times 10^{-6}$, simultaneously with the transition of damping into the non-linear range. The observed non-linear magnetic response of Fe is in qualitative agreement with results reported previously [13,33].

An important fact is that the non-linear anelasticity of the martensite is substantially more pronounced than that of the parent phase. This difference has traditionally been attributed to a high concentration of defects in the martensitic phase, created during the direct martensitic transformation. Usually, the high anelasticity of martensite is ascribed to the presence and high mobility of elastic domain boundaries, see e.g. Ref. [34]. As it has been mentioned before, in Ni–Mn–Ga single crystals there is a coherent rearrangement of elastic and magnetic domains [32] during macroscopic deformation. The present results indicate that the component of induction change, proportional to the anelastic strain just cannot be discerned in experimental data: the anelastic strain is strongly non-linear with respect to oscillatory stress amplitude, whereas the stress-induced induction is essentially linear. This fact indicates that the motion of magnetic and elastic domain boundaries is uncoupled in polycrystalline FMSA, and do not perform coherent oscillations. The difference between linear behaviour of stress-induced magnetization and non-linear anelasticity in poly-crystalline FMSA has been discussed in detail elsewhere [33]. It has also been shown that the non-linear anelasticity of polycrystalline FMSA is essentially insensitive to polarizing fields up to saturating values of around 1 T [8]. It has been suggested that both the absence of coupling between the motion of elastic and magnetic domains and the linearity of the magnetic domain wall displacement are associated with the existence of high internal stresses $\sigma_i$ in the polycrystalline Ni–Fe–Ga alloy. These alloys are brittle and, therefore, internal stresses induced during thermal treatment or martensitic transformation, cannot be efficiently relaxed by microplastic deformation. Apart from this source of high internal stresses, polyvariant martensitic samples are characterized by high values of stored elastic energy which can also make stress anisotropy predominant over the magnetocrystalline one [21]. If $\lambda_i \sigma_i > K$, where $K$ is the magnetocrystalline anisotropy constant, the configuration and the resistance of a magnetic domain wall to any change of its configuration is determined by the internal stress profile, rather than by magnetocrystalline anisotropy [1]. This leads, on one hand, to a lack of coupling of elastic and magnetic domains, which is supposed to be controlled by the magnetocrystalline anisotropy. On the other hand, effective internal stresses are known to strongly hinder the hysteretic motion of magnetic domain walls and thus suppress the hysteretic magnetostructural damping [1,35]. It is helpful also to estimate the values of stress anisotropy field produced by ultrasonic stress, Eq. (2). Taking $\lambda_i \approx 10^{-3}$, $\mu_0 M_s \approx 1$ T, $\sigma_0 \approx 2$ MPa, one obtains stress anisotropy field $H_a$ of only 30 A/m. In other words, in a sample with a high level of internal stresses, magnetic domain walls can perform, under rather low values of effective stress-induced magnetic anisotropy field $H_a$, only linear displacements within local potential minima.

5. Summary

We believe that mechanomagnetic spectroscopy offers a new method of direct investigation of magnetoelastic coupling in ferromagnetic materials. A few examples of application of this technique reveal a number of as yet unknown phenomena in ferromagnetic martensites and suggest new roles and interpretations for a variety of structural modifications existing in these materials.

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