Local elasticity and mobility of twin boundaries in martensitic films studied by atomic force acoustic microscopy

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Abstract

Nanoscale elastic properties of twinned martensite NiMnGa films were characterized by means of atomic force acoustic microscopy using cantilever contact-resonance spectra to measure the local contact stiffness \( k^* \) and the local damping \( Q^{-1} \), which contains information on the crystallographic anisotropy of martensitic twin variants and the dissipative motion of twin boundaries (TBs). Images of \( k^* \) and indentation modulus maps were obtained. Similar to topography images measured by conventional atomic force microscopy in contact mode, they show the nature of the twin structure and thus a regular variation in local elastic modulus. A correlation between \( k^* \) and \( Q^{-1} \) was observed and mirrors the motion of the TB accompanied by a viscoelastic procedure. The \( k^* \)-image and the topography image measured are opposite in contrast, which likely arises from mobile and immobile TBs depending on the geometry of twinning. Multi-resonance spectra were measured, which can be related to martensitic multivariants and are explainable as different types of nanotwins. A critical stress, defined as the starting point of softening due to TB movement was determined to be about 0.5 GPa for a thick film (1 \( \mu \)m) and 0.75 GPa for a thin film (0.15 \( \mu \)m), respectively. The values are much larger than that measured for bulk materials, but reasonable due to a large internal stress in the films.

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1. Introduction

The Ni$_2$MnGa compound is a technologically important material for its large magnetic shape memory (MSM) effect. The phenomenon refers to reversible displacements of the sample length up to 10% [1, 2] caused by the redistribution of martensitic variants via twin boundary (TB) motions under applied magnetic fields and/or mechanical stress with a hysteretic behavior [3]. The driving field is less than 1 T and the critical stress $\sigma_c$ is within 0.5–1.0 MPa for bulk materials [2–5]. The moderate driving field and the small critical stress are due to highly mobile TBs, particularly for layer-modulated orthorhombic martensite (5 or 7 M). In films it coexists often with non-modulated (NM) tetragonal martensite [6, 7]. The lattice modulation creates nanotwins with a period of a few nanometers and is visible by scanning tunnel microscopy (STM) [8] or by x-ray diffraction (XRD) measurements [2, 7]. The MSM effect operates well for bulk materials, but does not function so far for thin films on rigid substrates (except freestanding films). The TB motion is impeded by the internal stress arising from the film–substrate lattice misfit. A residual stress of about 50–250 MPa was reported for the films deposited on MgO [7, 9, 10] which is much larger than $\sigma_c$ measured for stress-free bulk materials. Another factor is the adhesion to the rigid substrate, which suppresses the reorientations of twin variants and thus impedes the MSM effect. Therefore, the intrinsic critical field for films remains unknown. The usage of atomic force acoustic microscopy (AFAM) provides, however, an opportunity to clarify the local movement of TBs and thus an unbiased critical stress $\sigma_c$ for MSM films. Because one can supply locally a large stress close to 1 GPa with the tip of the cantilever, this should be technically feasible.

AFAM combines ultrasonics with atomic force microscopy (AFM) [11–14]. It allows one to measure the local contact stiffness $k^*$ and with appropriate contact mechanics the local elasticity of samples on nanometer scales [14–18]. Longitudinal waves supplied by a waveform generator are injected into the sample making its surface vibrate and excite the cantilever beam to bending modes. The relevant contact mechanism can be approximately treated in connection of springs and dashpots, specified by $k^*$ and a local damping constant $\gamma^*$, respectively. The contact stiffness $k^*$ can be determined from the contact-resonance frequency $f_r$ of a given mode normalized to the free resonance frequency $f_0$ of the first mode

$$\frac{k^*}{k_c} = F\left(\frac{f_r}{f_0}\right)^2,$$

where $k_c$ is the stiffness of the cantilever. The function $F$ represents the dispersion curve of the motion of the cantilever under forced vibration. Generally, an increase of the contact stiffness $k^*$ shifts the resonance frequency to higher values and enhances the resonance amplitude $A_r$, while the local damping $\gamma^*$ broadens the resonance peak.

Since $\gamma^*$ is modeled as a dashpot whose loss is proportional to the time derivative of the cantilever amplitude at the position where the tip is fixed, i.e. to its velocity, it is not possible to obtain $Q^{-1}$ directly from the bandwidth of the resonance curve in the usual way (i.e. $Q_a^{-1} = \Delta f / f_r$ with $\Delta f$ denoted as the width of the resonance curve) since the cantilever is a mass-distributed system whose oscillatory amplitude varies along the cantilever. Instead it must be determined from the ratio of the imaginary part to the real part of the complex wave-vector of the corresponding cantilever mode and by separating the damping of the cantilever motion in air [19, 20]. As it turns out, there is a factor between $Q_a^{-1} = \Delta f / f_r$ and the local tip-sample damping $Q_{local}^{-1} = E'' / E'$ which depends on the geometrical parameters of the cantilever, on the contact-resonance frequency and on a factor which depends on the mode [21]. Here, $E''$ is the
local loss modulus and $E'$ is the local storage modulus. We show that the local viscoelasticity of the martensitic films is caused by the dissipative TB motion. On the system discussed here, contact-resonance measurements have also been made by Jakob et al [22] in order to measure the local indentation modulus and to compare its value with theoretical calculations.

Mapping the resonance amplitude $A_r$, which is performed by $x$–$y$ scanning with a fixed frequency near $f_r$, provides a $k^*$-image as a qualitative evaluation of the local elasticity. Similar to indenter experiments [23], the reduced contact modulus is given by

$$1/E^* = 1/M_t + 1/M_s,$$

(2)

where $M_t$ and $M_s$ are the indentation moduli of the tip and the sample, accounting for compressive and shear deformations in the contact zone. Furthermore, for a spherical tip or a flat punch, both of radius $R$, in contact with a flat surface, the relation of $k^*$ to the reduced modulus $E^*$ and the contact radius $a_c$ is given by

$$k^* = 2a_c E^*.$$

(3)

For a spherical tip $a_c = \sqrt{3PR/4E^*}$ and for a flat punch $a_c = R$. Taking a reference sample with known modulus, $E^*_{\text{ref}}$, the modulus $E^*$ of the sample can be quantitatively evaluated by a calibration procedure

$$E^* = E^*_{\text{ref}} (k^*/k^*_{\text{ref}})^n,$$

(4)

where $k^*_{\text{ref}}$ is the contact stiffness measured for the reference sample. For a spherical tip $n = 3/2$ and for a flat punch $n = 1$. Finally, for a spherical tip, the relation between $k^*$, $E^*$, tip radius $R$ and load $P$ is given by:

$$k^* = \sqrt[3]{6P/E^*^2}.$$

(5)

An increasing load $P$ increases the contact radius and consequently the contact stiffness $k^*$. Rough surfaces give rise to a geometry effect because of variations of the contact area and thus $k^*$. In this work, great attention has been paid to the surface corrugation caused by twinning. The corrugation is wavelike and is here referred to as twin lamellas of macrotwins. The relevant apexes and basins correspond to the TBs, which consist of coherent habit planes $\{110\}$ and separate the martensitic twin variants. Because of a large crystallographic anisotropy of martensitic NiMnGa compounds, as reported for example for a single crystal with Young’s moduli 11, 35 and 103 GPa in direction $\langle 100 \rangle$, $\langle 110 \rangle$ and $\langle 111 \rangle$ respectively [24], the $k^*$ value may change by reorientation of twin variants. For thin films, the indentation modulus was found to be about 151 GPa [25] and strongly depends upon deposition and annealing conditions [26] and thus quite differs from stress-free bulk materials. Furthermore, a NiMnGa alloy polymer composite was used to serve as a damping material for vibrations in the kHz range because the dissipative motion of TBs in this compound absorbs the vibrational energy [27, 28]. Here, we directly and locally measure the dissipation of the motion of TBs.

2. Experiments

Two MSM films of Ni$_{48}$Mn$_{28}$Ga$_{23$ (F1) and Ni$_{49}$Co$_3$Mn$_{25}$Ga$_{23$ (F2) used for AFAM experiments were epitaxially grown on MgO (100) substrates by dc-magnetron sputtering [7]. The film thickness, martensitic transition temperature $T_M$ and Curie temperature $T_C$ obtained by SQUID magnetometer (figure 1(a)) are listed in table 1. The film F2 is doped by 3 at.% Co to increase $T_M$ and $T_C$. As can be seen in figure 1, $T_M$ does not vary with applied magnetic field up to
Figure 1. Data for the magnetization $M$ obtained from transport measurements for the F1 film; (a) $M$ as a function of in-plane magnetic fields $H = 0.01, 0.2$ and $1 \text{T}$ respectively, showing the martensitic-austenitic transformation temperature $T_M$ and the Curie temperature $T_C$; and (b) $M(H)$ curves for the martensite ($-33$ and $27^\circ \text{C}$) and for the austenite ($57$ and $77^\circ \text{C}$).

Table 1. Parameters of the films used for AFAM experiments.

| Films | Concentration | Thickness (nm) | Twin lamella width/height (nm) | $T_M$ (°C) | $T_C$ (°C) |
|-------|---------------|----------------|-------------------------------|------------|------------|
| F1    | Ni$_{48}$Mn$_{28}$Ga$_{23}$ | 1000           | 155–175/1–1.5            | 37         | 102        |
| F2    | Ni$_{49}$Co$_3$Mn$_{25}$Ga$_{23}$ | 150            | 50–60/1–1.5             | 120        | 107        |

1 T and the magnetization curves (figure 1(b)) do not show a jump, demonstrating that a field-induced effect, such as the phase transformation or the reorientation of martensite variants, which occurs in bulk-samples, is suppressed by residual stress in the film and by its adhesion to the rigid substrate. The deposition temperature is $500^\circ \text{C}$ and thus the films grew with the parent phase L$_2^1$ (cubic austenite). A biaxial tensile stress exists in the films and is caused by a lattice mismatch (2.5% in diagonal) and by thermal expansion difference between the film and the substrate. The internal stress was found to be within 50–250 MPa, depending on the film thickness [7, 10]. It stabilizes the martensitic phase [9] and blocks the motion of TBs. Compared to the thin film F2, the thick film F1 is expected to show a lower residual stress and thus the unblocking of the TB motion is relatively easy.

It was observed by small angle x-ray scattering [7] that the film surface in the austenite state is very smooth with a roughness <0.5 nm, but in the martensitic state it becomes corrugated due to twinning. The twin lamellae were found to be aligned at $45^\circ$ to the substrate due to the epitaxial relation L$_2^1$(001)[110]//substrate(001)[100], where six {110} planes of L$_2^1$ serve as twin planes, four at $45^\circ$ and two at $90^\circ$ to the substrate. The width of twin lamellas of the macrotwins was measured to be 155–175 nm for F1 and 50–60 nm for F2 and is thus strongly...
thickness dependent. Their topography corrugation is within 1–1.5 nm, almost independent of the film thickness. The lattice structure was characterized by XRD. We found a mixture of NM and 7M martensite phases, i.e. twinned multivariants. The 7M martensite contains additionally nanotwins, which form also by shuffling \{110\} planes along the \langle110\rangle axis, five planes toward one direction and two neighbors toward the opposite direction. The period length amounts to 1.45 nm and a corresponding superlattice structure appears in relevant XDR patterns [7].

AFAM experiments were carried out by means of a Multimode AFM instrument from Veeco with a Nanoscope IV controller, provided with an ultrasonic transducer (center frequency 2.25 MHz) and a waveform generator. The sample was coupled to the transducer by an ultrasonic gel. AFM cantilevers \(k_c = 40 \text{ N m}^{-1}\) with silicon tips were used. Vibrations of the cantilever beam were detected by a position-sensitive detector, the same as usually used for surface topography measurements. Therefore, height images and ultrasonic images were obtained simultaneously in this manner. Contact-resonance spectra were determined by sweeping the generator frequency. The resonances occur in turn at different frequencies \(f_n\), where the subscript \(n = 1, 2, 3\ldots\) refers to the order of bending modes. We chose here the first mode, which is in our case in the range of 1.3–1.6 MHz and exhibits a sufficient \(\rho_f k^*\) sensitivity \((\alpha \partial f_r / \partial k^*, \text{given by the slope of the dispersion curve [11] and the magnitude of normalized contact stiffness } k^* / k_c, \text{here close to 30})\). The tip load is \(P = k_c d\), where \(d\) is the cantilever deflection created by the elongation of the scan piezoelectric element in \(z\) direction. The deflection is \(d = \beta \times V_d\) where \(V_d\) is the applied voltage to the piezoelement and \(\beta\) is the deflection sensitivity. A set-point of \(V_d = 0.5 \text{ V}\), corresponding to \(P \approx 0.38 \mu\text{N}\), was used to ensure a good tip-sample contact and thus a sufficient signal-to-noise ratio of the contact-resonances. To create a critical stress level \(\sigma_c\) necessary for TB motions, the static load dependence was measured by varying the set point \(V_d\) from zero to 1 V.

For calibration, we took the reference sample of SrTiO\(_3\) (STO) with a known indentation modulus of \(M_{\text{STO}} = 225 \text{ GPa}\) obtained from indenter experiments [29]. The silicon tips used have a modulus \(M_t\) of 165 GPa and an initial curvature radius \(R\) of 10–50 nm. In contact mode performance, \(R\) increases, however, due to wear until a limit value, typically up to 100 nm. This limit value allows reproducibility in collecting AFAM data. After the measurements, the form of the tip end was inspected by scanning electron microscopy. It looks sphere-like as can be seen in the inset of figure 2. Two tips were used for this work, one with \(R = 80\) nm (figure 2) and the other one with \(R = 100\) nm (not shown here). A larger \(R\) is expected to increase \(k^*\) and thus \(f_r\), according to equations (1) and (5). The contact radius \(a_c\) estimated from our data is less than 10 nm, which is necessary to spatially resolve the twin structure (macrotwins).

3. Results and discussions

3.1. Contact parameters

Figure 2 shows typical Lorentzian-shaped resonance spectra measured with the \(R = 80\) nm tip for STO and F1, including the free resonance \((f_0 = 0.296 \text{ MHz})\) of the cantilever itself. The contact-resonance maxima are located at 1.354 MHz for STO and 1.307 MHz for F1. Analyzing these data by equation (1) in the same way as in [17], we obtain the contact stiffness \(k_{\text{STO}}^* = 1.17 \text{ kN m}^{-1}\) for STO and \(k_{\text{F1}}^* = 1.04 \text{ kN m}^{-1}\) for F1, respectively. The reduced modulus \(E^*\) of the Si-STO is 95.2 GPa based on equation (2) using the data of \(M_{\text{STO}}\) and \(M_t\) given above. Based on equation (5), we expect a contact stiffness of 1.18 kN m\(^{-1}\) close to the experimental
value. Using equation (3), this entails \( a_c = 6.2 \) nm at an applied static force \( P = 0.38 \, \mu \text{N} \). The penetration depth \( \delta \) (\( \approx a_c^2 / R \)), which is defined as the vertical displacement of two points far away from the tip-surface contact, can be estimated to be about 0.45 nm. The parameters of \( a_c \) and \( \delta \) are a function of \( P \) and describe the size of the elastic deformation of the contact zone. The apparent damping factor \( Q^{-1}_a = \Delta f / f_r \) was found to be \( 0.71 \times 10^{-2} \) for STO. This results in \( Q_{\text{local}}^{-1} = E'' / E' = 0.88 \times 10^{-2} \) when applying the procedure mentioned above.

Furthermore, with the values of \( E_{\text{STO}}^* \) and \( k_{F1}^* \), the calibration equation (5) yields a reduced modulus \( E^* \) of about 79.7 GPa for the film F1. This gives an indentation modulus \( M_{F1} = 154 \) GPa, very close to the reported value of 151 GPa [25]. Accordingly, \( a_c \) and \( \delta \) were found to be 6.5 nm and 0.50 nm, respectively. The contact radius is less than the width of the twin lamellas of macrotwins. The relevant stress field, which decays with the distance from the sample surface, extends vertically up to a depth of about \( 3a_c \) [30], here about 19.5 nm in the film. This is small compared to the film thickness. Therefore, the evaluated modulus is not influenced by the substrate. The damping factor \( Q_{\text{local}}^{-1} \) measured for F1 amounts to \( 1.32 \times 10^{-2} \), corresponding to \( E'' / E' = 1.8 \times 10^{-2} \), larger than that for STO by a factor 2. This mirrors the viscoelastic behavior of the TB motion, see next paragraph.

### 3.2. Local damping and twin boundary motion

Several decades ago, there was a lot of work carried out on internal friction due to macro eddy-currents as well due to micro eddy-currents in ferromagnetic materials. They shed light on the dynamic processes in ferromagnetic materials. Micro-eddy currents are caused by single domain wall movements and lead to internal friction due to the resistivity of the material, see for example [31]. Here, we have the case of micro-eddy currents due to the motion of a single TB. Therefore, we expect that the full relaxation mechanism is operational and we can estimate the relaxation strength \( \Delta_{\text{max}} \) according to Mason [32]

\[
\Delta_{\text{max}} \approx \mu \mu_0 \lambda^2 E_s / M_s^2.
\]
Here, \( \lambda \) is the magnetostrictive constant, \( M_s \) is the saturation magnetization, \( \mu \mu_0 \) is the initial permeability and \( E_s \) is the Young’s modulus of the film. For an estimation, we take \( \lambda \approx 1.3 \times 10^{-4} \) \([33]\) and \( E_s = M_{F1}/(1 - \nu^2) \approx 136 \) GPa with Poisson’s ratio \( \nu \approx 1/3 \) and \( M_{F1} = 154 \) GPa measured for the film F1. Figure 1(b) gives \( M_s = 483 \) emu cm\(^{-3} \) (\( \approx 0.6 \) T) and \( \mu = 3.8 \) near the room temperature. Inserting these numbers into equation (6) yields \( \Delta_{\text{max}} \approx 3.1 \times 10^{-2} \). The corresponding \( Q^{-1} = \Delta_{\text{max}}/\pi \approx 10^{-2} \) is, given the uncertainties in the parameters entering equation (6), in line with our data \( Q_{a}^{-1} = 1.3 \times 10^{-2} \) for the film F1. More experiments and theoretical work are necessary in order to deepen the understanding of internal friction in MSM materials.

### 3.3. \( k^* \)-images of twinned martensite

The resonance signal was mapped by \( x-y \) scanning with a fixed resonance-frequency, giving a qualitative \( k^* \)-image. Figure 3(b) displays such a map obtained from the film F2, using the tip of \( R = 100 \) nm. Because of stripe-like twin lamellas, the F2 film is suitable both for \( x-y \) scanning and linear scanning specified below. A height image (\( h \)) was simultaneously obtained and is shown in figure 3(a) for comparison. The insert of figure 3 gives the corresponding resonance curve with a marker (red circle) at \( f_r = 1.50 \) MHz indicating the frequency used for mapping. Both \( h \)- and \( k^* \)- images demonstrate well the martensitic twin structure. The former gives the surface topography related to the twinning corrugation, while the latter indicates the local elastic moduli associated with the crystallographic anisotropy of the twin variants. Figure 3(c) shows line-scans across twin lamellas, the red curve from the \( h \)-image and the green one from the
$k^*$-image. They give the values of the twin width of about 50–60 nm and the height $h$ of about 1–1.5 nm, as well as the twin misorientation angle $\alpha \approx 2.3^\circ$. The $k^*$-image obviously shows a higher contrast than the $h$-image. More interestingly, however, the two images are almost opposite in contrast, although there is a small displacement in the line-scans of about 8 nm, as illustrated in figure 3(c). This result demonstrates that the stiffness $k^*$ of the lamella apexes is lower than that of the lamella basins. The result suggests a TB motion happening locally near the apexes under the stress supplied by the tip. The TBs near the lamella apexes seem to be mobile with respect to those (immobile) near the lamella basins.

To understand the opposite contrast of the $k^*$- and $h$-images, another $k^*$-image was measured for the same area, but with a lower frequency (1.47 MHz). The result is illustrated in figure 4(b), showing a contrast almost identical to the relevant $h$-image (figure 4(a)), as proven by the line-scans obtained across the twin stripes (figure 4(c)). The frequency 1.47 MHz is located on the left side at the half maximum (see insert of figure 4) and thus emphasizes the contrast for softer domains than in figure 3(b), namely for low $k^*$-regions observed near the apexes of the twin lamellas.

The result, namely that the contrast in the $k^*$-image inverses by changing the measurement frequency near the contact-resonance, indicates that the surface geometry effect is really insignificant. Actually, by scanning across the twin lamellas, the tip-sample contact area may change in form, but not in size. This is reasonable owing to a small $\alpha \approx 2.3^\circ$ for macrotwins and a confined $\delta(\approx 0.5 \text{ nm})$ in comparison to the twin height (1–1.5 nm). The contact zone may be elliptical, as can be deduced by contacting a corresponding sphere on a wavelike surface [30]. In this connection, the ellipse near the apexes possesses the long axis $a$ along the twin lamellae and the short axis $b$ is oriented perpendicularly, while near the lamella basins two axes mutually

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure4.png}
\caption{(a) AFM $h$-image; (b) AFAM $k^*$-image taken at 1.47 MHz (encircled in red in the inset) simultaneously measured for F2 (same scanned area shown in figure 3) and (c) line-scans across the twin lamellae: the red curve obtained along the red dashed line-scan in the $h$-image and the green one along the green dashed line in the $k^*$-image.}
\end{figure}
Figure 5. (a, b) Resonance spectra measured for F2 with a step size of 5.5 nm across the twin lamellae and fitted by Lorentzians (black curves); (c) the contact-resonance frequency $f_r$; (e) the amplitudes $A_r$; (d) the local damping factors $Q^{-1} = E''/E'$ as described above; and (f) the background signals were obtained from the spectra. The multi-resonances in (b) mirror the fact that the film contains martensitic multivariants, i.e. coexistence of 7M and NM martensitic phases.

Exchange. The contact radius is $a_c = (a + b)/2$ and the contact area remains approximately unchanged. From the relation $b = a \times \tan(45^\circ - \alpha)$, we get $b = 0.92a$.

3.4. Linear scanning across the twin lamellae

To get details of local elasticity, 50 resonance spectra were measured for F2 with a step spacing 5.5 nm across twin lamellae. We observed that about one half of the spectra exhibit a symmetrical distribution (figure 5(a)) centered at 1.533 MHz and well fitted by a Lorentzian. The other half of the spectra, however, displays multi-resonances as marked by 1, 2, 3, ... in figure 5(b). For these spectra, the Lorentz-fit yields a mean resonance maximum centered at 1.540 MHz. Multi-resonance spectra are expected to occur for multiphase samples, when the contact zone contains concurrently two or more phases. The result observed here is thus not surprising due to the coexistence of the NM and 7M martensite phases. The 7M possesses additionally nanotwins with a period of about 1.45 nm, which is less than $a_c$ and thus non-resolvable. The raised tiny twin lamellas (nanotwins) are visible by STM and appear alternatively on one of the twin variants of macrotwins, depending on orientations of twin planes either at 45° or 90° to the substrate [8]. The 45° type nanotwins are visible, since the twinning along a 45°-⟨110⟩ axis makes the film surface slightly raised. For this case, the force $P$ has a non-zero component perpendicular to TBs. It is equal to $P \times \cos45^\circ$ and sufficiently large to induce their motion. On the contrary, the twinning of 90° type nanotwins leaves the surface flat, and thus they are invisible. The relevant TBs move hardly because of a near
Figure 6. (a) Grid map \((300 \times 300 \text{ nm}^2)\) of indentation moduli \(M\) measured for F2 and calibrated by the reference sample STO with \(M_{\text{STO}} = 225\) GPa; (b) the number of data occurrences, showing two most probable values near 142 and 149 GPa, respectively; and (c) the average \( \bar{M} \) calculated by adding the data along the grid lines parallel to the diagonal and divided by the corresponding designated grid number.

zero-component of \(P\). The result of about the half spectra being multiresonance-like may be understood accordingly. The multiresonance spectra appear with relatively high frequencies and may arise from stiffer zones regarding the 90°-type nanotwins.

The Lorentz-fit yields the values of the resonance frequency, amplitude, width and offset of the resonance spectra, corresponding to \(f_r\), \(A_r\), apparent \(Q_a^{-1}\), and the background signal, respectively. These data are plotted versus the step distance in figures 5(c)–(f), respectively. The values for \(f_r\) (figure 5(c)) and \(A_r\) (figure 5(e)) depend on \(k^*\) and thus oscillate with twin lamellae of macrotwins. Low \(k^*\) values correlate with large \(Q_{\text{local}}^{-1}\) (figure 5(d)) when mobile TBs are scanned. The measured background signals (figure 5(f)) remain nearly constant with respect to the values of \(A_r\) given in figure 5(e) (same ordinate scale). This result further demonstrates that the surface geometry effect is minor.

3.5. Grid scanning

To map the local elastic moduli quantitatively, 10 \(\times\) 10 grid scans were made for the film F2 with a step size of 30 nm. The result is illustrated in figure 6(a), where the grid numbers indicate the scan sequence. The values of indentation modulus \(M\) scatter from 125 to 173 GPa, nevertheless there are two most probable values located near 142 and 149 GPa (figure 6(b)) corresponding to two twin variants of macrotwins. The 45° twin lamellas, which are not easy directly to recognize in the map, are able to clarify by average values (figure 6(c)) calculated by adding the data in figure 6(a) along the lines connecting the same grid number and divided by it. The average values oscillate with twin lamellas, similar to the result shown in figure 5(c). The magnitude of the indentation modulus \(M\) measured here agrees with the nanoindenter data measured for similar NiMnGa thin films [25, 26].
3.6. Static load dependence

Measurements of the contact-resonance frequency $f_r$, damping $E''/E'$, resonance amplitude $A_r$, and the background signal on the static load were carried out for F1 and F2 by varying the set-point $V_d$ from 0 to 1 V corresponding to static forces from 0 to 0.76 $\mu$N. The film F1 has a thickness of about 1 $\mu$m and a martensitic transition close to room temperature (see table 1). Figure 7(a) displays an AFM image measured for this film, showing a special twin structure. It looks grid-like and rather differs from the strip-like structure observed for F2 (figure 3). The grid-like twin structure indicates for thick films the alternative twinning along two mutually perpendicular $\langle 110 \rangle$ axes. The image profile is shown in figure 7(b) and gives the width of the twin lamellae of about 155–175 nm and the height of about 1–1.5 nm. The twin misorientation angle $\alpha$ is thus close to $1^\circ$, smaller than that of the film F2.

Figure 7(c) illustrates three resonance spectra obtained with static forces of 0, 0.46 and 0.76 $\mu$N, respectively ($V_d = 0, 0.6$ and 1.0 V). The contact-resonance frequency $f_r$ and the amplitude $A_r$ increases with $P$ in accordance with equation (5). Lorentzian fits were made for all spectra and the parameters obtained are plotted in figures 7(d)–(g). The background signal grows continuously with $P$, along a parabolic (or slight exponential) function and does not show a correlation with figures 7(d)–(f), indicating that the tip contacts well on the sample without a drift.
Figure 8. Load-dependent resonance frequency $f_r$ and damping $Q_{\text{local}}^{-1} = E''/E'$ measured for the thin film F2, showing a critical load near $P = 0.22 \mu N$.

Below a static force of about $P = 0.15 \mu N (V_d = 0.2 V)$, $f_r$ and $A_r$ increases approximately according to a cube-root-like function, whereas $Q_{\text{local}}^{-1}$ decreases. The cube-root dependence of $k^*$ on $P$ is actually given by equation (5), provided the modulus $E^*$ of the sample remains constant. Above $P = 0.15 \mu N$, however, the cube-root behavior does not hold anymore. The resonance frequency $f_r$ and the amplitude $A_r$ increase slowly with $P$, eventually reaching a plateau and then decreases, as can be seen in figures 7(d) and (f). The damping factor $Q_{\text{local}}^{-1}$ undergoes a minimum and then grows again. To explain this, we propose a decrease in $E^*$ due to a softening in the contact zone arising from stress-driven TB motion. The softening competes with stiffening upon loading and the latter becomes dominant when the load is above $0.53 \mu N (V_d = 0.7 V)$, accompanied with an again decreasing $Q_{\text{local}}^{-1}$ (figure 7(c)). In this connection, a critical stress $\sigma_c$ of about 0.5 GPa can be estimated by using the values $a_c \approx 10 \text{ nm}$ and $P \approx 0.15 \mu N$. The critical stress $\sigma_c$ seems to be much larger than that for bulk materials, which is in our view reasonable because of the large internal stresses (50–250 MPa) measured for the films.

A similar behavior was measured for the thin film F2 (see figure 8). A critical load occurs near $P = 0.22 \mu N$, where the local damping $Q_{\text{local}}^{-1}$ starts to rise and the resonance frequency $f_r$ increases slowly, though it does not reach a plateau. The critical stress is estimated to be $\sigma_c \approx 0.75 \text{ GPa}$ for F2. The value is higher than that measured for F1, reflecting the thickness dependence of the residual stress in the films [7, 10].

4. Conclusion

Local elastic properties were measured for twinned martensitic films of NiMnGa alloys by means of AFAM. Images of $k^*$ and indentation modulus maps on nanometer scales were obtained and demonstrate variations in local moduli regarding the mobility of TBs and/or the crystallographic anisotropy of twin variants. A correlation between $k^*$ and $Q^{-1}$ was observed, suggesting that the TB movement is dissipative and accompanied by a viscoelastic
behavior. Depending on the twin geometry, the TBs may be mobile at the lamella apexes and immobile at the basins, as is deduced from the observed inverted contrast between $k^*$- and topography images. Martensitic multivariants lead to the observation of multiresonance spectra, presumably concerning invisible $90^\circ$-twinned nanotwins. Static load-dependence measurements were carried out and a critical stress defined as the start of softening in the contact zone due to the TB motion was determined. The values are about 0.5 GPa for the $1\ \mu\text{m}$ film and 0.75 GPa for the $0.15\ \mu\text{m}$ film, respectively, and much larger than that measured for stress-free bulk materials.

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