Transformation twinning of Ni–Mn–Ga characterized with temperature-controlled atomic force microscopy

Matthew Reinhold,¹ Chad Watson,¹ William B. Knowlton,^{1,2} and Peter Müllner^{1,a)}

¹*Department of Materials Science and Engineering, Boise State University, Boise, Idaho 83725, USA*

²*Department of Electrical and Computer Engineering, Boise State University, Boise, Idaho 83725, USA*

(Received 16 December 2009; accepted 15 April 2010; published online 1 June 2010)

The magnetomechanical properties of ferromagnetic shape memory alloy Ni–Mn–Ga single crystals depend strongly on the twin microstructure, which can be modified through thermomagneto-mechanical training. Atomic force microscopy (AFM) and magnetic force microscopy (MFM) were used to characterize the evolution of twin microstructures during thermomechanical training of a Ni–Mn–Ga single crystal. Experiments were performed in the martensite phase at 25 °C and in the austenite phase at 55 °C. Two distinct twinning surface reliefs were observed at room temperature. At elevated temperature (55 °C), the surface relief of one twinning mode disappeared while the other relief remained unchanged. When cooled back to 25 °C, the twin surface relief recovered. The relief persisting at elevated temperature specifies the positions of twin boundaries that were present when the sample was polished prior to surface characterization. AFM and MFM following thermomechanical treatment provide a nondestructive method to identify the crystallographic orientation of each twin and of each twin boundary plane. Temperature dependent AFM and MFM experiments reveal the twinning history thereby establishing the technique as a unique predictive tool for revealing the path of the martensitic and reverse transformations of magnetic shape memory alloys. © 2010 American Institute of Physics. [doi:10.1063/1.3429090]

I. INTRODUCTION

Ni–Mn–Ga is a magnetic shape memory alloy (MSMA) with potential applications in sensor and actuator devices, magnetic refrigeration, power generation, and computer memory. The magnetic, mechanical, and magnetomechanical properties of Ni–Mn–Ga alloys depend strongly on the composition,^{1–3} martensite structure,^{4,5} twin microstructure,⁶ and temperature.^{7,8} The twin microstructure can be varied through suitable thermomechanical and thermomagnetic training.^{9,10} Without training, the martensitic transformation results in self-accommodated martensite with different martensite variants and many very thin ($<1\ \mu\text{m}$) twins. Such crystals display small magnetic-field-induced strain (MFIS) and do not fracture over very large numbers of magnetomechanical loading cycles. Well trained crystals contain only one martensite variant. Magnetic-field-induced and mechanically induced twins are thick, typically, $>10\ \mu\text{m}$.¹¹ These crystals display large MFIS and often fracture under cyclic magnetomechanical loading.⁶

Control of the twin microstructure during processing and in service (i.e., during ongoing cyclic magnetomechanical loading in a device) is critical for the performance of MSMA transducers. Control of the twin microstructure requires the experimental verification of the correlation between twin microstructure, active twinning modes—which are many in monoclinic 10M and 14M martensites^{12,13}—and MFIS. Non-destructive and spatially resolving methods for characterizing twinning modes will, thus, be instrumental for the development of fatigue-resistant MSMA transducers.

Electron backscatter diffraction (EBSD) was success-

fully applied to identify twinning modes in Ni–Mn–Ga.¹⁴ Although EBSD provides information about twin crystallography, it does not provide information about twin morphology below the surface, about shearing mechanics, and about the magnetic structure. While the surface relief morphology of twinned microstructures is intuitive and provides qualitative information, the quantitative interpretation of twin crystallography and twinning history is often ambiguous. Particularly, it is often not distinguishable whether the final relief at room temperature originates from the martensitic transformation upon cooling, from the reverse transformation upon heating, or from a combination of both. It was recently shown that the twin crystallography, the twin microstructure (including the morphology underneath the surface), and the magnetic domain structure of MSMA can be spatially resolved, nondestructively, with scanning probe microscopy.^{15,16} The aim of the present work is to demonstrate the identification of twin crystallography and twinning history via the combined use of atomic force microscopy (AFM) and magnetic force microscopy (MFM) *in situ* as a function of temperature, thereby revealing the transformation path.

II. TRANSFORMATION PATH AND SURFACE RELIEF

The transformation path is defined here as the selection of shear systems being facilitated through different twinning modes. The surface relief is dependent on the surface plane, the martensite structure, and the transformation path. Twinning causes a characteristic surface relief with planar slopes and sharp ridges and valleys. For the purpose of data analysis and theoretical interpretation, a naming convention was developed for the set of angles that result from twinning: twin-

^{a)}Electronic mail: petermullner@boisestate.edu.

TABLE I. Twinning angles φ_i for specific twinning systems in orthorhombic (14M) and tetragonal (10M) martensite calculated with Eq. (1) and using lattice parameter of Ref. 5.

Twinning angle	φ_a	φ_b	φ_c
Twinning	bc	ac	ab
Orthorhombic (14M)	2.7°	6.5°	3.7°
Tetragonal (10M)	$\dots$	3.6°	$\dots$

ning angles, relief angles, and slope angles. The angles between the normals of crystallographic (100), (010), and (001) planes of twin pairs are called *twinning angles* and given the symbol φ . The crystallography is based on the pseudotetragonal and pseudo-orthorhombic lattice axis systems for 10M and 14M martensite phases, respectively.^{17,18} Due to the lattice modulation, the symmetry of the unit cell is actually monoclinic. However, when referring to MFIS, the pseudo-orthorhombic and pseudotetragonal unit cells, which are derived from an orthogonal distortion of the cubic unit cell of the austenite phase, are more convenient. Therefore, we use these axis systems throughout this paper; where for convenience we drop the prefix “pseudo.” Consider, for example, the ac twinning mode, the twinning plane is (101). The lattice parameters a and c exchange positions across the twinning plane, which is parallel to the crystallographic b direction.^{15,19} The twinning angle, φ_b , is the angle between (100) in one twin and (001) in the other twin and is given by

$$\varphi_b = \arctan \frac{a}{c} - \arctan \frac{c}{a}, \quad (1)$$

where a , b , and c are the lattice parameters when using a orthorhombic or a tetragonal unit cell. The twinning angles φ_c and φ_a for ab and bc twinning follows from Eq. (1) by cyclic permutation of a , b , and c . Table I gives possible φ_i values for various twinning modes. Values for a , b , and c are taken from Sozinov *et al.*⁵

At surface relief valleys and ridges, the surface normals include the *relief angles* θ_V and θ_R , where the subscript V and R represent valleys and ridges. If the surface is parallel to the crystallographic (100)_{austenite} plane of the austenite, the relief angle equals one of the twinning angles (Fig. 1). This correlation is used here to evaluate twinning modes (which are described with twinning angles φ) from experimental surface data (i.e., θ angles).

FIG. 1. Schematic illustrating the relief produced on a (100)_{austenite} surface by ac twinning. This is a cross-section of a twin perpendicular to the y direction. The orientation of the orthorhombic unit cell is indicated. The thick black lines are twin boundaries. The twin sequence is CAC (the letters indicate which crystallographic direction is perpendicular to the surface) and the relief angle and twinning angle are equal, $\theta = \varphi_b$.

FIG. 2. (a) The ac twin found in Fig. 1(a) after polishing and (b) at a temperature above the martensitic transformation where a double kink appears at the position of the former A twin domain. The relief angles are equal and opposite to the relief angles in Fig. 1.

Multiple twinning events may occur even during one heating and cooling experiment. As a result, the surface relief will contain multiple sets of valleys and ridges. It is useful to define the *slope angle*, σ , as the angle between the normals of the local surface plane and the macroscopic surface plane. The slope angle is the experimentally accessible quantity. Furthermore, the martensitic phase transformation may generate different variants, thus, forming twins with different orientations. The angular mismatch between the relief ridges and valleys of each twinning plane with a different orientation is denoted as β (e.g., caption to Fig. 9).

The relief angles may deviate from the twinning angles listed in Table I even when the surface is parallel to (100)_{austenite}. To illustrate the variety of possible surface reliefs, a thought experiment is presented here. Assume a surface contains a relief due to ac twinning as schematically shown in Fig. 1. Individual twin domains are labeled A and C according to the crystallographic directions a and c , which are perpendicular to the surface. Now the surface is polished perfectly flat [i.e., the twin relief is removed as in Fig. 2(a)]. Upon heating through the martensitic-austenite transformation, the twin boundaries disappear. A surface relief is now formed [Fig. 2(b)] with angles equal and opposite to those in Fig. 1.

Upon cooling through the martensitic transformation, there are various surface relief development options, which depend on twinning mode, twin plane orientation, and twinning sequence (i.e., the order of twin variants, e.g., CAC in Fig. 1). There are four possible mechanisms for ac twinning upon cooling when assuming that the twin boundaries appear at the same positions before and after heating. In the first situation, the same twinning planes and the same twinning sequence may reoccur, i.e., the twin structure returns to its initial configuration. Thus, the final relief angle is zero [Fig. 3(a)]. Second, the twinning sequence may change from CAC to ACA while the twin boundary orientation stays as before, i.e., inclined to the lower left. The change in twinning sequence reverses the shear direction. Thus, the relief angle doubles to $\theta = 2\varphi_b$ [Fig. 3(b)]. In the third option, the twinning plane may change from inclined to the lower left to inclined to the lower right. This also results in a doubling of the final relief angle $\theta = 2\varphi_b$ [Fig. 3(c)]. The fourth possibility

FIG. 3. Reliefs generated on a (100)_{austenite} surface by different transformation paths through *ac* twinning when cooling from the situation shown in Fig. 2(b). (a) Twinning on the same planes as in Fig. 2(a) and the same twin sequence ACA changes the relief angle by $-\varphi_b$ and results in a flat surface; (b) reversal of the twin sequence to ACA increases the relief angle by $+\varphi_b$ to a total relief angle of $\theta=2\varphi_b$; (c) changing the twinning planes also doubles the final relief angle when keeping the sequence CAC; and (d) changing both the twinning sequence (from CAC to ACA) and the twinning plane orientation results in a flat surface.

is that the twinning plane and twinning sequence may change and the relief angle will flatten to zero [Fig. 3(d)]. The surface relief pattern of situations 1 and 4 [Figs. 3(a) and 3(d)] and of situations 2 and 3 [Figs. 3(b) and 3(c)], respectively, are identical even though the corresponding twin arrangements are different. Thus, two different twin arrangements exist for each surface relief pattern.

In the above thought experiment, the same twinning mode, which was present before heating, reappears during cooling. If the twinning sequence changes from CAC to CBC, the relief angle will be reduced by $-\varphi_a$ during cooling so that the final relief angle equals the difference $\theta=\varphi_b-\varphi_a$ [Fig. 4(a)]. Second, the twinning sequence may become BCB and the relief angle will change by $+\varphi_a$ during cooling to a total angle $\theta=\varphi_b+\varphi_a$ [Fig. 4(b)]. Third, for twinning on twinning planes inclined to the lower right and a CBC twinning sequence, the relief angle will change to $\theta=\varphi_b+\varphi_a$ [Fig. 4(c)]. The fourth possibility is that the twinning plane orientation may change and the twinning sequence becomes BCB. In this case, the relief angle equals the difference $\theta=\varphi_b-\varphi_a$ [Fig. 4(d)]. Again, two different twin arrangements exist for each surface relief pattern.

Other possibilities upon cooling [Fig. 2(b)] include twins that do not form and relief angles equal to φ_b . Furthermore, all twinning modes may occur with the traces of the twinning planes at different positions. The corresponding relief angles equal φ_a , φ_b , and φ_c . Table II lists all possible relief angles starting with one twinning type before thermomechanical treatment and upon cooling the same twinning type remains or different twinning types appear. The probability of each twinning event depends on extrinsic factors including external magnetic fields, mechanical loading, and structural imperfections such as inclusions, pores, etc.

It is evident from this thought experiment that additional

FIG. 4. Reliefs generated on a (100)_{austenite} surface by different transformation paths with *bc* twinning upon cooling when starting from the situation shown in Fig. 2(b). (a) Twin sequence CBC and the same twin plane orientation as before heating leads to a final relief angle $\theta=\varphi_b-\varphi_a$; (b) twin sequence BCB and the same twin plane orientation as before heating leads to a final relief angle of $\theta=\varphi_b+\varphi_a$; (c) twin sequence CBC with a different twinning plane orientation results in $\theta=\varphi_b+\varphi_a$; and (d) twin sequence BCB with twinning planes inclined to the right results in $\theta=\varphi_b-\varphi_a$.

information is required to identify the various possible outcomes. In this paper, it is shown that by combining AFM and MFM, with *in situ* AFM heating experiments, it is possible to resolve the twinning crystallography and to some extent the twinning history of a MSMA crystal and the transformation path.

III. EXPERIMENTAL

A cuboidal sample of Ni₅₀Mn₂₉Ga₂₁ (numbers indicate atomic percent) single crystal with faces parallel to (100), comprised of martensite structures 10M and 14M,¹⁵ was spark eroded from a crystal grown following the Bridgman technique. The transformation temperatures were determined with low-field magnetization measurements using a vibrating sample magnetometer (Model 10, ADE Technologies, Westwood, MA). The martensite start and finish temperatures are 43 °C and 42 °C, respectively, while the austenite start and finish temperatures are 46 °C and 48 °C, respectively. The

TABLE II. Total relief angles θ going from twinning mode 1 to twinning mode 2 (or vice versa) upon heating and cooling for surface planes parallel to (100)_{austenite}. The relief angles are $\theta=\varphi_i \pm \varphi_j$ with $i, j=a, b, c$, the sign is positive for additive shear and negative for subtractive shear.

Structure	Twinning mode 1	Twinning mode 2	Relief angle θ for additive shear (deg)	Relief angle θ for subtractive shear (deg)
Tetragonal (10 M)	<i>ac</i>	<i>ac</i>	7.2	0.0
Orthorhombic (14 M)	<i>ab</i>	<i>ab</i>	7.4	0.0
	<i>bc</i>	<i>bc</i>	5.4	0.0
	<i>ac</i>	<i>ac</i>	13	0.0
	<i>ab</i>	<i>ac</i>	10.2	2.8
	<i>bc</i>	<i>ac</i>	9.2	3.8
	<i>ab</i>	<i>bc</i>	6.4	1.0

FIG. 5. Loading geometry for the thermomechanical treatment. The sample was compressed parallel to the shortest edge which is the x direction. Cartesian coordinates were defined as indicated. The crystallographic c direction is parallel to the x axis over most of the sample. There are two possibilities for the orientation of the crystallographic a and b directions. The AFM and MFM experiments were performed on the shaded surface normal to the y axis.

Curie temperature is 98 °C. Cartesian coordinates were defined with the short, mid, and long edges parallel to the x , y , and z directions (Fig. 5). The x - z face was polished at room temperature (i.e., with the sample being fully martensitic) with a 1 μm diamond slurry and finished with an acidic aluminum oxide slurry. The finely polished surface exhibited a surface roughness of 2 nm root mean square as determined with AFM from three square areas measuring $10 \times 10 \mu\text{m}^2$. To relieve the twins created during sample preparation, the sample was thermomechanically treated after the surface was polished as follows. The sample was heated to 130 °C, where the sample is fully austenitic. During heating and cooling, a constant load of 12 ± 4 MPa was applied in the x direction. This was done to align the crystallographic c direction parallel to the direction of the applied force. The crystallographic a and b directions align predominantly and with equal probability parallel to the y and z directions.^{20,21}

An AFM system (Dimension 3100, Nanoscope V Controller and Heater-Cooler Accessory, Veeco Metrology, Inc., Santa Barbara, California) was used to characterize the surface relief and the magnetic structure of the surface at 25 °C (where the sample is fully martensitic) and at 55 °C (where the sample is fully austenitic). The surface relief was imaged in ac mode using a ferromagnetic tip coated with CrCo (MESP, Veeco Instruments, Inc., Camarillo, CA). The magnetization vector of the tip was parallel to the tip axis and perpendicular to the sample surface. MFM images were taken first at 25 °C (in the martensite phase), then at 55 °C (in the austenite phase), and finally again at 25 °C. The temperature during imaging was controlled with a thermoelectric heating-cooling unit. The higher temperature was chosen such that the Ni-Mn-Ga sample would be in the austenite phase yet clearly below the Curie temperature of 98 °C. After the AFM/MFM characterization, x-ray diffraction experiments were performed with a Bruker AXS D8 discover diffractometer using a $\text{Cu } K_\alpha$ source. The diffraction experiments were performed on the surface which was characterized with the AFM/MFM and revealed the 10M martensite structure with lattice parameters $a = 5.960 \pm 0.005$ Å and $c = 5.596 \pm 0.002$ Å, yielding a c/a ratio of 0.939 ± 0.002 .

FIG. 6. Representative (a) AFM height image, (b) amplitude error image, and (c) MFM magnetic image of the xz face showing surface relief bands taken at room temperature. In the amplitude error image, the three shades of gray each indicate areas of relatively equivalent slope values. The strong contrast of the magnetic image indicates out-of-plane magnetization while the weak (neutral) contrast indicates in-plane magnetization (Ref. 15). The angle, β (defined in b), between the surface relief bands measures 8.4°.

The Ni-Mn-Ga sample was adhered to a 6 mm stainless steel puck with silver paint (Leitsilber 200, Ted Pella, Inc., Redding, CA). To further enhance thermal coupling, a thin layer of thermal paste was applied between the stainless steel puck/sample assembly and the thermoelectric stage. To prevent condensation on the cold cantilever at the elevated temperature, a positive pressure of high purity nitrogen gas was maintained within a silicone rubber seal enveloping the cantilever and sample. Three calibration runs were performed to determine the appropriate temperature setpoint for a sample temperature of 55 °C. Prior to imaging, the sample was held at 55 °C for 20 min to reach thermal equilibrium. Optimal imaging was obtained with a scan rate of 1.0 to 1.2 Hz and a lift height of 75 nm.

IV. RESULTS

Following thermomechanical treatment, two sets of parallel surface relief bands approximately parallel to the z direction were observed on the polished xz face. Both sets appear on the height image [Fig. 6(a)] and on the amplitude error image [Fig. 6(b)]. The amplitude error image displays the difference between the amplitude setpoint and the actual amplitude of the cantilever oscillation. The contrast of the amplitude error image is proportional to the surface slope. The surface reliefs have piecewise constant contrast and, thus, are piecewise planar. The surface has different slopes where bands intersect. The angle, β [defined in Fig. 6(b)], between these bands measures 8.4°. In the MFM phase image [Fig. 6(c)], only one set of bands exhibit alternating strong (black and white) and weak (gray) contrast. Strong black and white contrast indicates that the magnetic moments point into (black) and out-of (white) the surface. Weak gray contrast indicates that the magnetic moments are parallel to the surface. The magnetic moments are coupled to the direction of easy magnetization, which is the crystallographic c direction.²² Thus, the MFM image [Fig. 6(c)] shows that the corresponding set of surface relief bands originates from crystallographic twins where the crystallo-

FIG. 7. Representative (a) AFM height image, (b) amplitude error image, and (c) MFM magnetic image of the surface relief at 55 °C. (d) A 15 μm cross-section of the surface with a relief angle $\theta_{H13} = 4.3^\circ \pm 0.2^\circ$ [the subscript H3 refers to the labeling in Fig. 8(b)]. The position of the cross-section (d) is marked with a white line in (a). Regions R1 and R2 point out an uncommon trait found in this image. Most often similar twin domains have parallel and equivalent slope values (i.e., $\sigma_1 = 2.1^\circ$ for R1 and $\sigma_2 = 3.0^\circ$ for R2). Thus, the difference between the slopes of R1 and R2 is 0.9° .

graphic c direction alternates from parallel to the surface (i.e., weak contrast) to perpendicular to the surface (i.e., strong contrast).¹⁵ The second set of surface relief bands that appears with the lightest gray shade in Fig. 6(b) does not appear in the MFM image [Fig. 6(c)]. Thus, the crystallographic c direction does not change across ridges and valleys of the corresponding surface relief.²³

Figures 7(a)–7(c) are the height image, amplitude error image, and magnetic image of the xz face at 55 °C, which is in the paramagnetic austenite phase. The height [Fig. 7(a)] and amplitude error [Fig. 7(b)] images show one set of surface relief bands. These bands coincide with the lightest gray bands recorded at 25 °C that did not show magnetic contrast [compare Figs. 6(b) and 7(b)]. The set of surface relief bands that did show magnetic contrast at 25 °C disappeared during heating. Figure 7(d) is a 15 μm cross-section taken at the white line on Fig. 7(a). Two regions, R1 and R2, marked in Fig. 7(d), have different slope angles, namely, $\sigma_1 = 2.1^\circ$ for R1 and $\sigma_2 = 3.0^\circ$ for R2. Dissimilar slopes are uncommon. Additionally, in Fig. 7(c), there is no change in the magnetic pattern over the entire image.

V. INTERPRETATION

To illustrate the correlation of one set of surface relief bands to the magnetic domain structure, the amplitude error image [Fig. 6(b)], and the MFM image [Fig. 6(c)], both recorded at 25 °C, are overlaid in Fig. 8(a). The ridges and valleys are marked with solid lines and the slopes between these ridges and valleys are labeled A and B. Bands A and B have a weak and strong magnetic contrast indicating that they represent crystallographic twins. In Fig. 8(b), the ridges and valleys of the second set of surface relief bands are marked with dashed lines and the corresponding slopes are labeled K and L. The magnetic contrast is identical for K and L, which would agree with ab twinning but not with ac and bc twinning.¹⁵

FIG. 8. (a) AFM amplitude error image is overlaid with a small section of the MFM magnetic image to define the location of the P twin boundaries. P_e ($e=1,2,3,\dots,9$ from left to right) indicate the names of each P twin boundary. The twin domains alternate from A to B to A across each boundary. (b) AFM amplitude error image with H twin boundaries defined. H_f ($f=1,2,3,4$ from left to right) indicate the names of each H twin boundary. The twin domains alternate from K to L to K across each boundary.

Upon heating, the AB surface relief disappeared while surface relief KL remained. Therefore, the ridges and valleys of A and B slopes are twin boundaries, which disappear with the transition from the martensite to the austenite phase. These twins are termed “present twins” (P) since they are actually present at room temperature. In contrast, the ridges and valleys of K and L slopes do not represent existing crystallographic twins. The origin of the KL relief is related to “historic” twins (H), which were present during sample preparation (as detailed in the thought experiment within Sec. II).

The ridges and valleys of the P and H twins are labeled P_e ($e=1,2,3,4,\dots,9$) and H_f ($f=1,2,3,4$), respectively, on the height image (Fig. 9). The slope angles (σ_{AK} , σ_{AL} , σ_{BK} , and σ_{BL} , subscripts refer to the slopes on each side of the ridge/valley) were measured from one ridge/valley to the next and at 90° with respect to the corresponding ridge and valley. The slope angles from five cross-sections were averaged for each P and H twin. Each slope angle was compared

FIG. 9. The combination of Figs. 8(a) and 8(b) onto the AFM height image. The solid black lines mark P twin boundaries and the long dashed black lines mark H twin boundaries. Lines 1–5 (dotted lines) indicate cross-sections used to measure the slope angles for the H twins and lines 6–10 (short dashed line) indicate cross-sections used to measure the slope angles for the P twins. The angle (β) between the traces of H and P twins measures 8.4° . Labels are as defined in Fig. 8.

TABLE III. Slope angles σ and relief θ angles for the H and P twinning events. The subscript letters stand for H, P, and the areas as described in Fig. 8. The values for the relief angles (last four rows) were obtained with Eqs. (2)–(5).

Relief angle	Average angle (deg)	Standard deviation (deg)
$\sigma_{AK,H}$	0.19	0.23
$\sigma_{BK,H}$	−3.56	0.22
$\sigma_{AL,H}$	4.87	0.17
$\sigma_{BL,H}$	0.29	0.14
$\sigma_{AK,P}$	0.26	0.24
$\sigma_{BK,P}$	−3.67	0.18
$\sigma_{AL,P}$	4.91	0.20
$\sigma_{BL,P}$	0.33	0.20
θ_{HV}	4.68	0.40
θ_{HR}	3.85	0.36
θ_{PR}	4.58	0.41
θ_{PV}	3.93	0.42

to other slope angles within the same P and H twinning domains. Two H relief angles (θ_{HV} and θ_{HR}), and two P relief angles (θ_{PV} and θ_{PR}) were identified by

$$\theta_{HV} = \sigma_{AL} - \sigma_{AK}, \quad (2)$$

$$\theta_{HR} = \sigma_{BL} - \sigma_{BK}, \quad (3)$$

$$\theta_{PR} = \sigma_{AL} - \sigma_{BL}, \quad (4)$$

$$\theta_{PV} = \sigma_{AK} - \sigma_{BK}. \quad (5)$$

The H relief angles were evaluated within a single P twinning domain. Similarly, the P relief angles were evaluated within a single H twinning domain. After heating to the austenite phase (55 °C) and cooling to the martensite phase (25 °C), the P twins reappeared at the same positions and angles. Table III lists all results and standard deviations.

VI. DISCUSSION

With the combination of AFM and MFM experiments, it is possible to identify the twin microstructure of Ni–Mn–Ga single crystals in the martensite phase. The values for the relief angles θ_H and θ_P are between 3.8° and 4.7° (Table III) and deviate from the values of the twinning angles given in Table I. This may partly be attributed to the statistical variation of about 10% (column 4 of Table III). The deviation may also originate from the lattice parameters, which depend on composition.^{3,24} The values in Table I were calculated for c/a (10M) and b/a (14M) ratios of 0.939 (taken from x-ray diffraction results) and 0.937, respectively.⁵ For comparison, for a ratio of 0.93,²⁵ the relief angle is 4.2°, which is the average of the angles (θ_P) measured for the P twins, and within a standard deviation of the individual experimental values (Table III). Thus, the deviation from the values in Table I may be due to variations in the lattice parameters. The MFM images show that the crystallographic c direction changes across the twin boundaries, which excludes ab twinning. Within the experimental error, the relief angles match with the twinning angle for ac twinning in 10M martensite.

The H twins appear as a persistent surface relief. A possible mechanism for the formation of a persistent surface relief was described with Fig. 2. To reiterate, the relief angle suggests ac twinning. These twins were formed prior to polishing (i.e., during a heating-cooling cycle preceding polishing). After polishing, the surface was flat yet the crystal contained ac twins. When heated after polishing, the high-temperature relief [Fig. 2(b)] was formed. Upon the final cooling, the transformation path differed from the transformation path that took place on the cooling prior to polishing. Therefore, twinning did not occur on systems with twinning planes emerging at the ridges and valleys that were present at 55 °C. Thus, the surface relief of the martensite phase (after cooling) displays the twin microstructure that was present before heating the sample to the austenite phase. The last cooling prior to surface polishing was performed without imposed stress and without magnetic field, which results in a self-accommodated martensite with many twins on various hierarchical levels. After polishing, the sample was heated and cooled under a stress of about 12 MPa, which is sufficient to train the crystal.²⁶ Thus, the twin microstructure changes from when the sample was polished (i.e., H twins) to when it was analyzed with AFM/MFM (i.e., P twins).

There is an 8.4° angle (β) between the traces of the H twin boundaries (H_f , thin-dashed lines in Fig. 9) and those of the P twins (P_e , thin solid lines in Fig. 9). This angle indicates that the H twins had formed in a differently oriented martensite variant. The nucleation of martensite variants is a strong function of extrinsic forces such as mechanical load and magnetic field. As for the occurrence of a persistent surface relief, the different thermomechanical treatments performed prior to and after polishing are most likely responsible for the angle between P twins and historical twins.

Upon heating to the austenite phase, the magnetic contrast disappears, even though the material is ferromagnetic. This indicates that the very weak magnetic anisotropy of the austenite phase is not sufficient to significantly affect the domain pattern. The magnetic moments align parallel to the free-surface to minimize the magnetostatic energy.

The success of AFM/MFM as a nondestructive predictive method for revealing twin crystallography and twinning history originates from leveraging magnetocrystalline anisotropy and transformation strains. This method may also be applied to other materials with strong magnetocrystalline anisotropy and polytwinned microstructures²⁷ and with phase transformations leading to crystallographic domains or twinning [e.g., massive and shear transformations in Mn–Al (Refs. 28 and 29)]. Furthermore, this method may be extended to ferroelectrics with the use of piezoforce microscopy. By analogy, an electric field induced by a conductive AFM tip on twinned ferroelectric ceramics may be used to determine its twin crystallography.³⁰

VII. CONCLUSIONS

The conclusions of this study may be summarized as follows.

- The twin crystallography can be identified by a com-

bination of AFM and MFM from the relief angles and the magnetic domain structure.

- The accuracy of this method relies on knowing the lattice parameters.
- Variable temperature AFM/MFM experiments reveal the twinning history. Twinning modes which operated during previous thermomagnetomechanical training events can be identified.
- The domain structure in the weakly anisotropic ferromagnetic austenite phase was not revealed with the high-temperature MFM experiments.
- Variable temperature AFM/MFM provides a nondestructive predictive method for characterizing twin crystallography and the transformation path of magnetic shape memory alloys. This method can be applied to other polytwinned ferromagnetic materials and, analogously, also to twinned ferroelectric materials.

ACKNOWLEDGMENTS

We thank Cassie Witherspoon for performing the XRD experiment and Adrian Rothenbuhler for performing the VSM experiment. We acknowledge partial financial support through DARPA Contract No. N66001-01-C-80345, NIH Grant No. P20 RR016454 from the INBRE Program of the National Center for Research Resources, NSF MRI Award DMR 0619795, and NSF MRI Grant Award 0216312. We acknowledge Veeco Instruments Inc. for the use of a “before market” prototype of the Veeco Heater-Cooler Accessory and Veeco’s engineering support.

¹V. A. Chernenko, E. Cesari, V. V. Kokorin, and I. N. Vitenko, *Scr. Metall. Mater.* **33**, 1239 (1995).

²V. A. Chernenko, *Scr. Mater.* **40**, 523 (1999).

³O. Heczko and L. Straka, *J. Magn. Magn. Mater.* **272–276**, 2045 (2004).

⁴V. A. Chernenko, P. Müllner, M. Wollgarten, J. Pons, and G. Kosterz, *J. Phys. IV* **112**, 951 (2003).

⁵A. Sozinov, A. A. Likhachev, and K. Ullakko, *IEEE Trans. Magn.* **38**, 2814 (2002).

⁶M. Chmielusz, V. A. Chernenko, W. B. Knowlton, G. Kosterz, and P. Müllner, *Eur. Phys. J. Spec. Top.* **158**, 79 (2008).

⁷L. Straka, O. Heczko, and S. P. Hannula, *Scr. Mater.* **54**, 1497 (2006).

⁸N. Okamoto, T. Fukuda, and T. Kakeshita, *Mater. Sci. Eng., A* **481**, 306 (2008).

⁹S. J. Murray, M. Marioni, S. M. Allen, R. C. O’Handley, and T. A. Lograsso, *Appl. Phys. Lett.* **77**, 886 (2000).

¹⁰P. Müllner and G. Kosterz, *Mater. Sci. Forum* **583**, 43 (2008).

¹¹L. Straka, O. Heczko, and H. Hanninen, *Acta Mater.* **56**, 5492 (2008).

¹²P. Müllner, D. Mukherji, M. Aguirre, R. Erni, and G. Kosterz, *Micromechanics of Magnetic-Field-Induced Twin-Boundary Motion in Ni-Mn-Ga Magnetic Shape-Memory Alloys* (The Minerals, Metals & Materials Society, Phoenix, AZ, 2005), p. 171–185.

¹³M. Han and F. F. Kong, *J. Alloys Compd.* **458**, 218 (2008).

¹⁴A. Koblishka-Veneva, C. Gachot, P. Leibenguth, and F. Mücklich, *J. Magn. Magn. Mater.* **316**, e431 (2007).

¹⁵P. Müllner, Z. Clark, L. Kenoyer, W. B. Knowlton, and G. Kosterz, *Mater. Sci. Eng., A* **481**, 66 (2008).

¹⁶M. Reinhold, D. Kiener, W. B. Knowlton, G. Dehm, and P. Müllner, *J. Appl. Phys.* **106**, 053906 (2009).

¹⁷J. Pons, V. A. Chernenko, R. Santamarta, and E. Cesari, *Acta Mater.* **48**, 3027 (2000).

¹⁸Y. Ge, O. Söderberg, N. Lanska, A. Sozinov, K. Ullakko, and V. K. Lindroos, *J. Phys. IV* **112**, 921 (2003).

¹⁹N. Lanska and K. Ullakko, *J. Phys. IV* **112**, 925 (2003).

²⁰A. L. Roytburd, *Phase Transitions* **45**, 1 (1993).

²¹A. L. Roytburd, *J. Appl. Phys.* **83**, 228 (1998).

²²R. Tickle and R. D. James, *J. Magn. Magn. Mater.* **195**, 627 (1999).

²³G. Fritsch, V. V. Kokorin, V. A. Chernenko, A. Kempf, and I. K. Zaslachuk, *Phase Transitions* **57**, 233 (1996).

²⁴M. Richard, J. Feuchtwanger, D. Schlager, T. Lograsso, S. M. Allen, and R. C. O’Handley, *Scr. Mater.* **54**, 1797 (2006).

²⁵P. Müllner, V. A. Chernenko, and G. Kosterz, *J. Appl. Phys.* **95**, 1531 (2004).

²⁶P. Müllner, A. V. Chernenko, D. Mukherji, and G. Kosterz, *MRS Symp. Proc.* **785**, 415 (2004).

²⁷N. I. Vlasova, G. S. Kandaurova, and N. N. Shchegoleva, *Phys. Met. Metallogr.* **90**, 239 (2000).

²⁸C. Yanar, J. M. K. Wiezorek, V. Radmilovic, and W. A. Soffa, *Metall. Mater. Trans. A* **33**, 2413 (2002).

²⁹A. S. Sologubenko, P. Müllner, H. Heinrich, and G. Kosterz, *Z. Metallkd.* **95**, 486 (2004).

³⁰G. Arlt, *J. Mater. Sci.* **25**, 2655 (1990).