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**Neutron Diffraction Study of NiTi during Compressive Deformation
and after Shape-Memory Recovery**

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Abstract Neutron diffraction measurements of internal elastic strains and texture were performed during compressive deformation of martensitic NiTi deforming by twinning. Rietveld refinement of the diffraction spectrum was performed in order to obtain lattice parameter variations and preferred orientation of martensitic variants. The elastic internal strains, are proportional to the externally applied stress but strongly dependent on crystallographic orientation. Plastic deformation by matrix twinning is consistent with type I (1-1-1) twinning, whereby (100) and (011) planes tend to align perpendicular and parallel to the stress axis, respectively. The preferred orientation ratio r according to the model by March and Dollase is proportional to the macroscopic plastic strain for (100) and (011) planes for loading, unloading and shape-memory recovery. To the best of our knowledge, this is the first in situ bulk measurement of reversible twinning in NiTi. Finally, shape-memory recovery results in a marked change of NiTi cell parameters.

1. INTRODUCTION

The thermoelastic phase transformation of NiTi from an ordered, high-temperature cubic phase B2 (austenite) to an ordered, low-temperature monoclinic phase B19' (martensite) deforming by twinning is responsible for the shape-memory effect exhibited by these alloys (see, e.g., Ref. { ADDIN } [1]{ ADDIN }). Stress-free martensite consists of equal proportions of the 24 possible crystallographic variants with different orientations, as a result of self-accommodation during transformation, which minimizes the internal transformation strains. Upon deformation, the variant with the largest strain in the direction of the applied stress grows at the expense of the other, less favorably oriented variants. This twinning deformation results in a preferred orientation in the martensite and a macroscopic strain. This strain can be recovered by heating the twinned structure into the austenite stability region. If upon subsequent cooling equal proportions of the 24 variants are again formed, the strain recovery is conserved (shape-memory effect).

As diffraction techniques can accurately measure lattice strains, they are well suited to study materials containing residual stresses or subjected to external stresses. Furthermore, diffraction techniques are sensitive to crystal structure and orientation, thus allowing the investigation of materials exhibiting twinning and phase transformations, such as shape-memory alloys. Thermal neutrons have a penetration depth in the range of millimeters in NiTi, as compared to a typical value of less than 10 μm for X-Rays { ADDIN } [2]{ ADDIN }. Thus, neutrons probe the volume of the NiTi material, while X-Rays are limited to its surface, where the state of stress (and thus the microstructure for thermoelastic NiTi) in a tensile or compression test is not always representative for that of the bulk.

In this paper, we present a neutron diffraction study of the internal strains and orientation in martensitic NiTi, both during compressive deformation by twinning and after subsequent shape-memory recovery. The crystallography of variant conversion is also investigated.

2. EXPERIMENTAL PROCEDURES

As described in more detail in another publication { ADDIN } [3]{ ADDIN }, a NiTi specimen was fabricated by vacuum hot pressing of prealloyed NiTi powders (99.9% pure, 70 μm average size, from Special Metals Corp., NY), from which a cylindrical compression sample (9.9 mm in diameter and 24 mm in height) was fabricated by electro-discharge machining. To minimize residual stresses and solutionize the matrix, the sample was annealed under titanium-gettered, flowing argon for 1 h at 930 $^{\circ}\text{C}$, furnace-cooled to 400 $^{\circ}\text{C}$ and air-cooled to room-temperature. All sample transformation temperatures are above room-temperature and the density is 99.5% of the theoretical value { ADDIN } [3]{ ADDIN }.

Diffraction measurements were performed with the Neutron Powder Diffractometer at the Manuel Lujan Jr. Neutron Scattering Center (Los Alamos National Laboratory, New Mexico) which operates a pulsed neutron source and a time of flight spectrometer. A customized mechanical tester was used to load the sample in uniaxial compression with the loading axis forming an angle of 45 $^{\circ}$ with the incident neutron beam, as described in Ref. { ADDIN } [4]{ ADDIN }. Diffraction spectra were measured simultaneously by two detectors at angles of -90 $^{\circ}$ (diffraction vector Q parallel to load) and +90 $^{\circ}$ (diffraction vector Q perpendicular to load) with respect to the incident beam, measuring reflections from lattice planes perpendicular and parallel to the load axis, respectively. Bragg reflections with lattice spacings between 0.5 \AA to about 4 \AA were recorded and each spectrum was normalized with the total incident fluency.

Two 3-mm strain-gauges attached on diametrical sides of the sample recorded the macroscopic strain; for strains above 1%, cross-head displacement was used. Diffraction measurements were performed at increasing uniaxial compressive stresses of -3 MPa, -90 MPa, -210 MPa and -280 MPa, corresponding to a maximum macroscopic strain of up to 1.6% (Fig. 1). Further measurements were made during unloading at stresses of -100 MPa and -3 MPa. Some relaxation was recorded after each stress change, which was held under load control while diffraction data were collected for about 4 hours. Since the magnitude of the relaxation was relatively small (see Fig. 1) and the test was operated under load control maintained constant, relaxation is not considered to affect the measurements. After the mechanical loading cycle, the sample was removed from the mechanical tester, recovered for 5 minutes in an oil bath held between 150 and 175 °C (significantly above the A_f temperature) and cooled to room temperature. The sample, which had recovered about 77% of the plastic strain (Fig. 1), was again subjected to diffraction measurements at a nominal stress of -3 MPa.

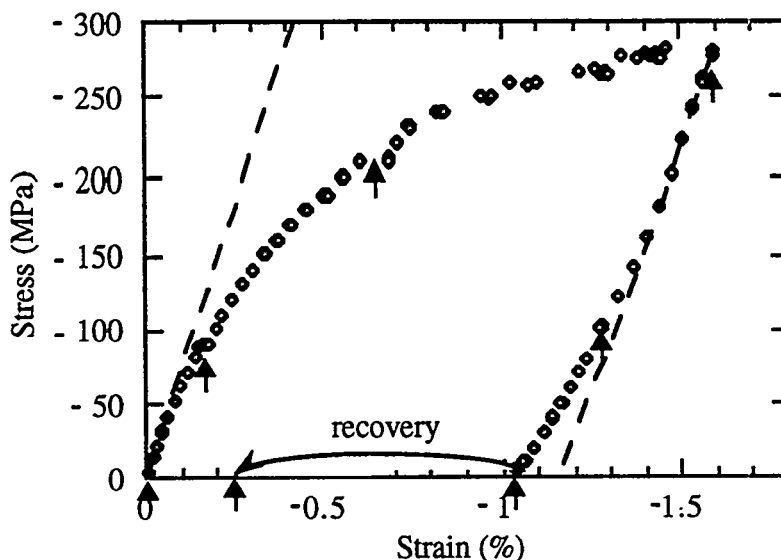


Figure 1: Measured compressive stress-strain curve of NiTi. The strain levels at which the diffraction measurements were taken are indicated with arrows. The strain recovery is also shown on the strain axis.

The lattice spacings d_{hkl} for the set of planes hkl determined through Bragg's relationship exhibited a shift Δd under stress, from which the elastic strain ϵ_{hkl} was calculated:

$$\left\{ \text{EMBED "Equation" * mergeformat} \right\} \quad (1)$$

where d_0 is the reference plane spacing measured in the undeformed sample. The assumption that the undeformed sample is stress-free is justified in Ref. { ADDIN }[5]{ ADDIN } where the thermal and transformation residual strains are shown to be negligible. Furthermore, the average sample response under stress was determined using the Rietveld approach, whereby the intensities and positions of all Bragg peaks are predicted using an assumed crystal structure { ADDIN }[6]{ ADDIN }. Analysis was performed using the Los Alamos Generalized Structure Analysis System (GSAS) program { ADDIN }[7]{ ADDIN }. The mean phase strains were then calculated using Eq. (1) from lattice parameters determined by Rietveld refinement. Also measured were the intensities of individual Bragg peaks, which correlate with the fraction of NiTi variants in the diffraction condition. A normalized scale factor was calculated as the ratio of a peak intensity to its intensity under no applied stress. Finally, a special procedure of the GSAS program based on the formulation by March { ADDIN }[8]{ ADDIN } and Dollase { ADDIN }[9]{ ADDIN } was used to quantify the preferred orientation of (100) and (011) planes. The parameter defined by these authors as the preferred orientation ratio r characterizes the ellipticity of the distribution of oriented platelike crystals assuming a spherical distribution for random orientation.

3. RESULTS AND DISCUSSION

The Rietveld procedure on the undeformed NiTi diffraction spectrum (Fig. 2) gives the best fit with the $P112_1/m$ monoclinic structure, confirming the generally admitted structure { ADDIN }[10,11]{ ADDIN }. In disagreement with the neutron diffraction results by Ref. { ADDIN }[12]{ ADDIN }, no match with the $P2/c$ structure was found. Crystallographic data of the undeformed sample are given in Table 1, with c as the unique axis of the monoclinic cell.

Table 1: Lattice parameter and relative atom positions

parameter	a (Å)	b (Å)	c (Å)	γ (°)
undeformed	$2.90392 \pm 2 \cdot 10^{-4}$	$4.66116 \pm 3 \cdot 10^{-4}$	$4.11777 \pm 2 \cdot 10^{-4}$	$97.740 \pm 6 \cdot 10^{-3}$
recovered	$2.90351 \pm 3 \cdot 10^{-4}$	$4.65671 \pm 5 \cdot 10^{-4}$	$4.12177 \pm 3 \cdot 10^{-4}$	$97.531 \pm 1 \cdot 10^{-2}$
atom position (undeformed)	x	y	z	
Ni	$0.9638 \pm 7 \cdot 10^{-4}$	$0.8236 \pm 4 \cdot 10^{-4}$	0.25	
Ti	$0.5726 \pm 19 \cdot 10^{-4}$	$0.2804 \pm 9 \cdot 10^{-4}$	0.25	

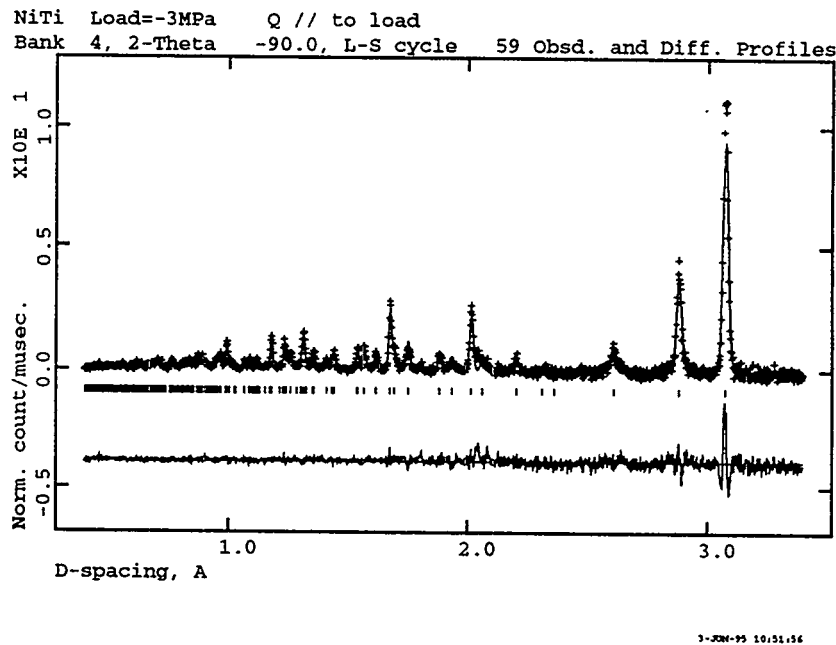


Figure 2: Neutron diffraction spectrum of NiTi before deformation (Q parallel to load), and Rietveld refinement fit.

Figure 3 shows the normalized scale factors of the most intense, overlap-free Bragg reflections (100) and (011) as a function of the plastic strain (obtained by subtracting the elastic strain from the total strain (Fig. 1)) during mechanical loading, during unloading and after recovery. Upon loading, the intensity of (100) planes perpendicular to the load axis increases while that of (011) planes decreases. The opposite behavior is observed for planes parallel to the load axis. We conclude that variant coalescence produces preferential orientation of (100) planes perpendicular (respectively of (011) planes parallel) to the compressive load axis. An analysis of crystal geometry given in Ref. { ADDIN }[5]{ ADDIN } indicates that the above observations can be explained by (1-1-1) type I twinning { ADDIN }[13]{ ADDIN }; because the (100) and

(011) planes are almost symmetric with respect to the (1-1-1) plane, type I twinning leads to the replacement of (100) planes in diffraction position with (011) and vice versa.

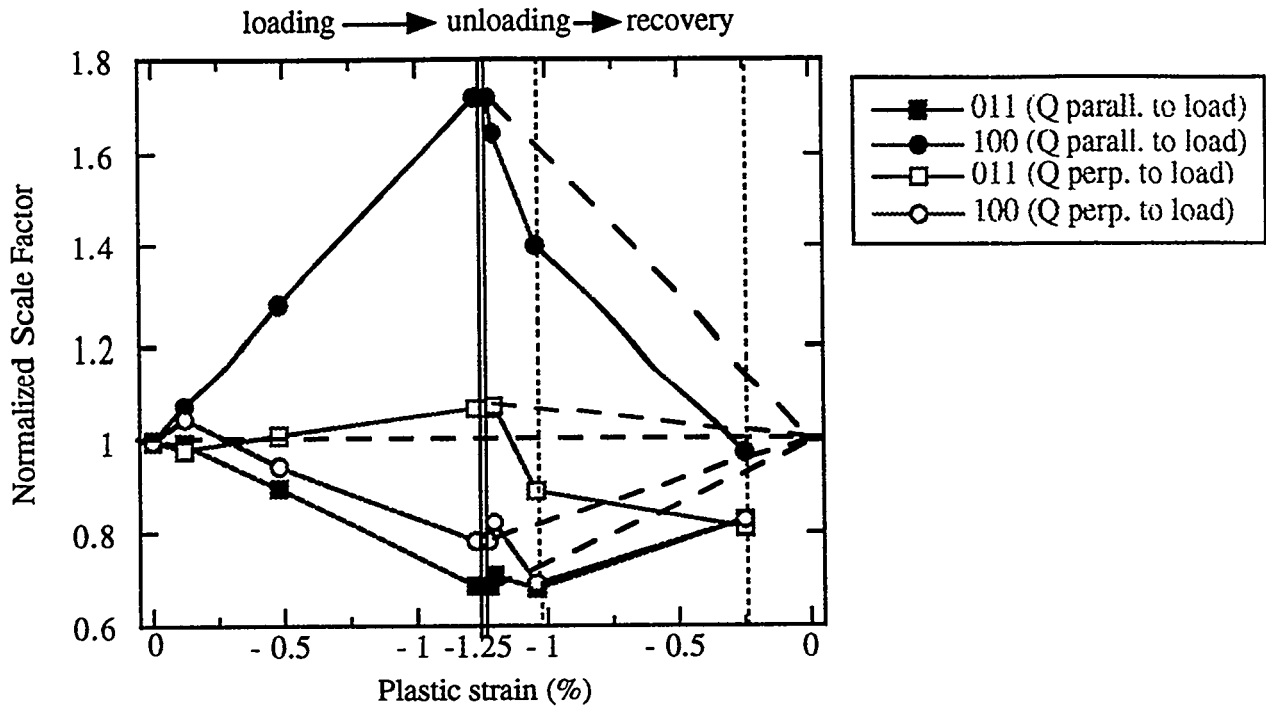


Figure 3: Normalized scale factors of the (100) and (011) planes of NiTi as a function of the plastic strain during loading, during unloading and after recovery, for diffraction spectra with scatter vector Q parallel and perpendicular to the load.

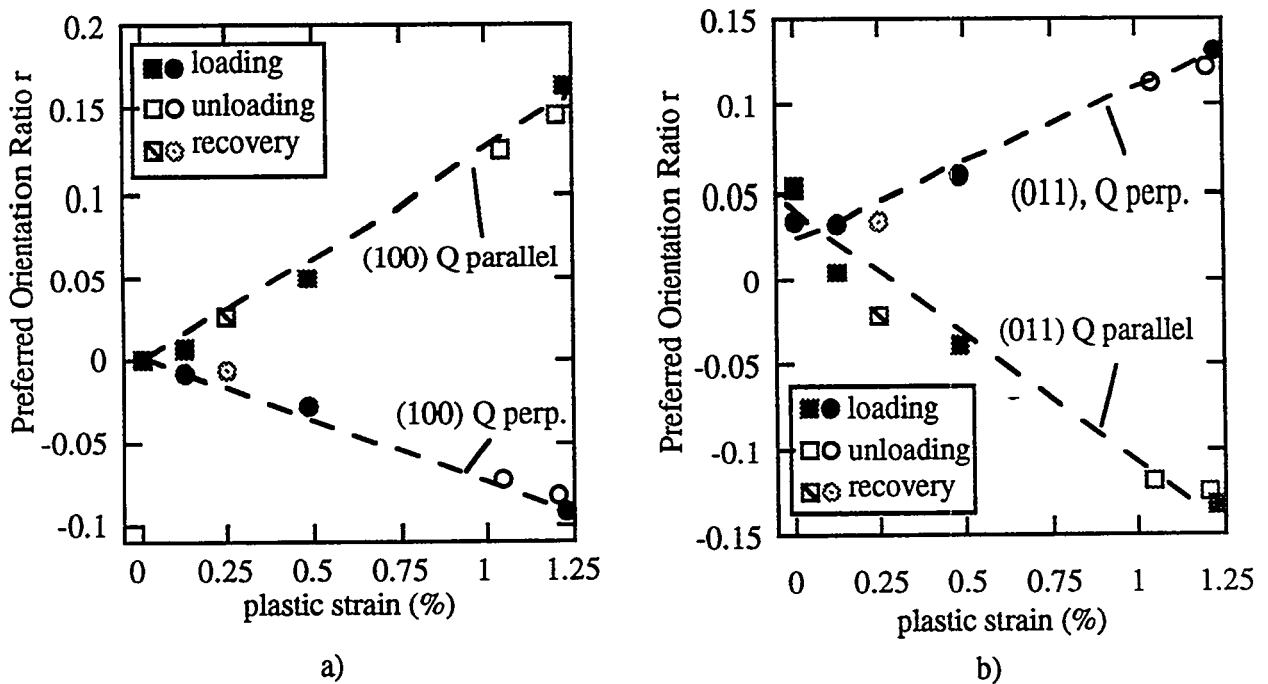


Figure 4: Reorientation ratio of (100) planes (a) and (011) (b) for scatter vectors Q parallel and perpendicular to the load axis as a function of plastic strain during loading, during unloading and after recovery.

In Fig. 4, the preferred orientation ratio r (from the Rietveld refinement) is plotted as a function of the plastic strain (from strain-gauge macroscopic measurements). For all stages of deformation (loading, unloading and recovery), the relationship between these two strains is linear, demonstrating that the March-Dollase model successfully describes NiTi deformation by reorientation. To the best of our knowledge this is the first time this model is applied to martensite plate twinning. While the exact physical meaning of the relation between r and plastic strain needs to be clarified, the present experiments show that r is directly proportional to the fraction of reoriented martensite plates. Furthermore, we note that Fig. 3 displays a linear relationship between normalized scale factors and plastic strain for loading only, but not for unloading and after shape-memory recovery. The discrepancy between the trends in Fig. 3 and 4 is probably due to scatter of single peak refinement. This comparison illustrates the ability of the Rietveld refinement procedure to average experimental scatter, by using the entire diffraction spectrum.

As shown in Fig. 1, the unloading portion of the stress-strain curve is not linear, indicative of rubberlike behavior. Figure 4 confirm that detwinning for (100) planes is taking place in a manner reversible with respect to the macroscopic strain, for loading and unloading. The same is true for the shape-memory recovery. Based on observation of variant motion on polished samples, it is widely accepted that reversible twinning is responsible for the rubberlike and shape-memory recovery. However, since the stress state at the surface is different from that in the bulk and since variant behavior is very sensitive to stress, these observations do not positively prove that detwinning is reversible in the bulk. We believe that the observations reported in the present paper are the first direct measurement *in the bulk* of the reversibility of twinning upon mechanical unloading and shape-memory recovery. Finally, the symmetric behavior of (100) and (011) planes also confirms that type I (1-1-1) twinning is responsible for martensitic crystal reorientation.

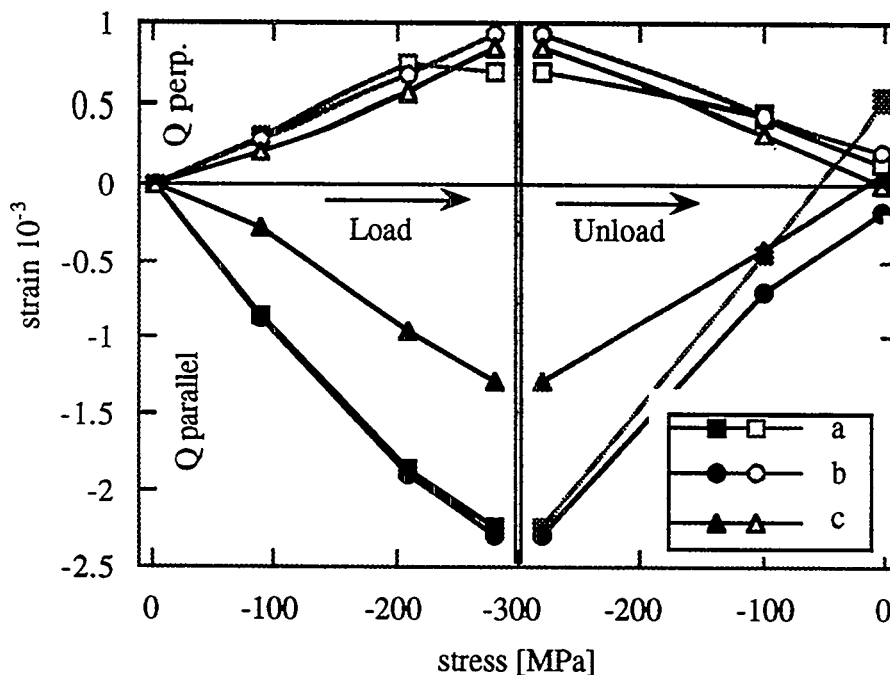


Figure 5: Strain parallel and perpendicular to load axis along the a, b and c directions of the monoclinic cell as a function of applied stress during loading and unloading.

Figure 5 shows the strain determined along the {100}, {010} and {001} directions (a, b, c directions in the monoclinic cell) as a function of applied stress. As expected, a near linear behavior is found upon both loading and unloading. The elastic moduli along the three crystal directions, defined as the slope of the lines in Fig. 5 for strains parallel to the load axis, are significantly higher than the Young's modulus, $E=60-70$ GPa, determined from the macroscopic stress-strain curve (Fig. 1). The values measured by neutrons are constrained moduli which can partly explain this difference. However, as described in more details in another paper { ADDIN }[5]{ ADDIN }, the most significant contribution to decrease the macroscopic polycrystallin

Young's modulus comes from the shear constant C_{44} (20-30 GPa Brill et al.] which is anomalously low for martensitic NiTi near the phase transformation temperature [14]. The data shows that NiTi is elastically anisotropic, as also observed considering individual plane reflections in Ref. [5]. The ratio between perpendicular and parallel elastic strains are in rough agreement with the value of NiTi Poisson's ratio $\nu=0.42$ [14], except for the c axis. After unloading, a slight tensile residual stress exists for (100) planes in the direction parallel to the load axis. Because many (100) planes result from twinning (Figs. 3 and 4), some residual elastic tensile back-stress are indeed expected after unloading. On the other hand, no residual stress is measured for the (100) planes perpendicular to the loading axis. Since the diffracting (100) planes after unloading are not twinned and were already in diffraction position in the before deformation, residual stresses are likely to be low. Finally, crystallographic lattice parameters are significantly different after recovery from those measured both in the undeformed and unloaded states (Table 1). Measurements for individual Bragg reflections however show that the residual strains after shape-memory recovery are very low [5], indicating that the discrepancy in lattice parameters is not due to residual stresses. Since the lattice parameters are practically the same in both measured directions, the discrepancy is not due to an artefact of the Rietveld fit procedure or to a mispositioning of the sample. We thus conclude that shape-memory recovery results in a significant change in the equilibrium lattice cell for the {010} and {001} directions and the monoclinic angle γ (Table 1).

4. CONCLUSIONS

1. Rietveld refinement of neutron diffraction data allows a precise evaluation of lattice parameters of monoclinic martensitic NiTi undergoing compressive uniaxial deformation.
2. Reorientation and coalescence of variants is measured *in situ* in bulk NiTi during twinning deformation: (100) planes orient perpendicular to the load axis and (011) planes parallel to the load axis, in agreement with type I (1-1-1) twinning.
3. The preferred orientation ratio r according to the model by March [8] and Dollase [9] is proportional to the macroscopic plastic strain for (100) and (011) planes. To the best of our knowledge, this is the first time this approach is applied to martensite twinning.
4. The lattice elastic moduli of NiTi are anisotropic and significantly higher than the bulk Young's modulus.
5. After shape-memory recovery, a change of the NiTi lattice parameters is observed.

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