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Elastic constants of non-modulated Ni-Mn-Ga martensite

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ABSTRACT

Room temperature elastic constants of non-modulated (NM) tetragonal martensite of a Mn-rich Ni-Mn-Ga alloy were determined by ultrasonic methods. The results are in good qualitative agreement with ab-initio predictions and confirm that NM martensite exhibits strong elastic anisotropy with shear instability related to the soft acoustic phonons mediating the reverse transition. The geometric arrangement of the softest shearing modes is shown to be identical as for the stress-induced *fct* martensite of the Fe-31.2 at.%Pd alloy. However, it markedly differs from the arrangement of the soft shearing modes in parent Ni-Mn-Ga austenite phase.

In shape memory alloys (SMAs), the transitions between the high temperature phase (austenite) and the low temperature phase (martensite) is mediated by soft acoustic phonons [1]. In the cubic austenite phase, the softest acoustic phonons typically correspond to shearing of the cubic lattice along the Bain path; this soft shear is a [1–10] (110) shear represented by the elastic constant $c' = (c_{11} - c_{12})/2$, where c_{ij} are the elastic constants of the austenite in Voigt's notation. Numerous shape memory alloys have been shown to have particularly small c' coefficients indicating this phonon instability, e.g. Cu-Al-Ni [2], Cu-Zn-Al [3], Fe-Pd [4], Co-Ni-Al [5] and Ni-Mn-Ga [6,7,8]. For martensites, however, the spatial arrangement of the soft shearing modes of the lattice is much less understood, as the full elastic tensors for only few SMAs in the martensite phase are known. In particular, González-Comas et al. [3] determined all elastic constants of 18R monoclinic martensite of Cu-Zn-Al by the ultrasonic pulse-echo method, and Sedlák et al. [2] used the same method for orthorhombic 2H martensite of Cu-Al-Ni. The results for this alloy were further refined by Landa et al. [9] using resonant ultrasound spectroscopy. Dai et al. [10,11], applied a thickness resonance method for determination of the elastic constants of monoclinic 10M martensite of Ni-Mn-Ga in a tetragonal approximation. All these experiments have shown that also the martensite phases exhibit some soft shearing modes, but no general conclusions could be drawn on the relation between these shear modes and the geometric parameters of the respective transitions and on the relation to the soft modes of the parent phase. Moreover, in all these cases, the studied martensites were *modulated* (18R, 2H and 10M) and exhibiting, consequently, a lower symmetry class than tetragonal. The tetragonal case is, however, the most important as it corresponds to a simple Bain distortion.

In this letter, we report on elastic constants of non-modulated (NM) Ni-Mn-Ga martensite, which is a tetragonal phase related to the austenite phase by a Bain distortion with $c/a > 1$. The Ni-Mn-Ga alloy is one of the most intensively studied SMAs nowadays, as the 10M (5M in older notation) modulated Ni-Mn-Ga martensite exhibits extremely small twinning stress and high mobility of the twin interfaces [12,13]. According to the adaptive concept of martensite [14,15], the 10M structure can be understood as a nano-laminate of the NM martensite phase with a specific stacking sequence; hence, the effective elastic properties of the 10M phase can be expected to follow directly from the elastic constants of the NM phase. Several first-principles calculations of the elastic constants of NM martensite [16,17,18] confirmed strong shear instability along specific shearing planes, but no experimental validation of these theoretical results has been reported so far.

The examined material was a single crystal of a Ni50.5-Mn30.4-Ga19.1 alloy exhibiting the NM structure with lattice parameters $c = 0.660$ nm and $b = a = 0.547$ nm ($c/a = 1.207$) at room temperature. The crystal was originally in a multi-variant state, but was reoriented into a dominantly single variant state by applying a 40 MPa uniaxial tension along the [001] direction. Details on this approach for preparation of a single variant state of NM martensite and its characterization by X-ray pole figure measurements can be found in [19]. The magnetic measurement done on the same sample [20] and particularly the optical microscopy observations indicated that there was still a very small volume fraction of other variants remaining in the sample, visible at the largest face of the sample as thin lamellae inclined by 45° from the [001] direction. Owing to their small amount (~2 vol%), the presence of these lamellae was not expected to affect significantly the macroscopic elastic constants of the material. As we will show later, the material exhibited very strong tetragonal elastic anisotropy, while any non-negligible volume fraction of another variant in form of such a laminate

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would lead to monoclinization of the elastic behavior. The sample was a $5.46 \times 4.75 \times 3.43$ mm^3 non-rectangular parallelepiped; exact crystallographic orientations of the faces of the sample were obtained by X-ray Laue's method. The mass density was determined as $\rho = 8.12$ g·cm^{-3} by Archimedes method.

The elastic constants of the sample were determined at room temperature by resonant ultrasound spectroscopy (RUS [22,23]) complemented by pulse-echo ultrasonic measurements of velocity of longitudinal waves in three directions perpendicular to the faces of the sample. As shown in [9,21], such a combination of RUS and pulse-echo measurements enables reliable determination of all independent elastic coefficients for an anisotropic material of arbitrary symmetry class. The RUS method is based on measurements of resonant spectra of free elastic vibrations of the sample; the elastic constants themselves are then obtained by solving an inverse problem, i.e. by minimizing the misfit between the measured resonant frequencies and the resonant frequencies of the same vibrational modes calculated for iteratively refined guesses of the elastic constants. With the pulse-echo results involved, also the misfit between the measured and calculated values of phase velocity of longitudinal waves in given directions is simultaneously minimized, and thus the precision of the coefficient determination is increased [21].

The measurements were performed using the contact-less laser-based RUS apparatus described in [21] at room temperature (22 °C, stabilized with accuracy ± 0.05 °C). The experiments were done in zero external magnetic field. As shown by Heczko et al. [24], the magneto-elastic coupling in NM martensite is very weak and external field up to 1 T resulting in magnetic saturation has no measurable effect on the RUS spectra.

The examined material was assumed to exhibit tetragonal elastic anisotropy (symmetry class I, point group *D4h*), which is fully described by six independent elastic constants. For x_3 being the tetragonal axis, these constants are c_{11}, c_{12}, c_{13}, c_{33}, c_{44} and c_{66}. Total number of 32 resonant modes in the frequency range 120–600 kHz was used for the inverse procedure; for the final optimized set of elastic constants, all these modes were fitted with accuracy better than 3 kHz. This suggests that the chosen tetragonal symmetry class well describes the real behavior of the material. The resulting elastic constants are listed in Table 1 and compared with ab-initio predictions. While the constants c_{11} and c_{12} are somehow overestimated by the ab-initio calculations, for all other constants the agreement between the experiment and the theoretical predictions is strikingly good.

Most importantly, it is directly seen that the NM martensite exhibits very strong elastic anisotropy in shear constants, as $c_{44} \sim 2c_{66}$ and $c_{13} \sim 2c_{12}$, while the anisotropy of the longitudinal elastic constants is much weaker ($c_{11} \sim c_{33}$). In Fig. 1(a–c), the results are visualized in the usual form of planar cuts of phase velocity surfaces (cf. [2,3,9]). The phase velocity v_φ of elastic waves propagating in direction $\mathbf{n}$ is related with the elastic constants C_{ijkl} by Christoffel's secular equation

$$\det\left(C_{ijkl}n_j n_l - \rho v_\varphi^2 \delta_{ik}\right) = 0, \quad (1)$$

where ρ is the mass density and δ_{ik} is the Kronecker's symbol. For each $\mathbf{n}$, this equation has up to three solutions, corresponding to three different modes of propagation. One mode (usually the fastest) has quasi-longitudinal polarization (denoted qL), the remaining two modes have quasi-transverse polarizations (the faster denoted as qT1 and the slower as qT2). The plots of $v_\varphi(\mathbf{n})$ for $\mathbf{n}$ running over a unit sphere are the *phase velocity surfaces*, and the minima at the qT2 phase velocity surface indicate the soft shearing modes of the lattice, corresponding to the softest acoustic phonons that mediate the transition [25].

As the tetragonal symmetry (class I) was assumed for the processing of the RUS data, the phase velocity surfaces in Fig. 1(a–c) also exhibit this symmetry, characterized by $(100)_M$, $(010)_M$, $(110)_M$, and $(001)_M$ mirror planes, where the subscript M denotes that the Miller indices refer to the martensite lattice. To verify independently that the material indeed exhibits this symmetry class, the same input RUS data were processed assuming that the material is of the lowest possible symmetry, i.e. triclinic with all 21 independent elastic constants (cf. [21]). Due to the larger number of the sought parameters, the inverse calculation gave results with much higher uncertainty for all c_{ij}-s (typically ± 10 GPa). In Fig. 1(a–c), the phase velocity surfaces for the resulting set of 21 elastic constants are plotted by dash-dot lines. It is apparent that the tetragonal symmetry is approximately obeyed also by these surfaces. Especially the qT2 surface, which is the one most accurately determined by RUS, shows only a negligible misfit between results with and without assuming tetragonal symmetry; the matching is excellent in particular in regions close to the minima at the qT2 surface. Hence, we can conclude with certainty that the examined material indeed exhibited tetragonal symmetry with strong elastic anisotropy and the presence of the small amount of other martensitic variants did not affect the result more than within the experimental error range. Consequently, the minima at the qT2 surfaces seen in Fig. 1(a–c) can be used for discussion of the soft shearing modes and soft acoustic phonons in the NM martensite.

For comparison, Fig. 1(d) shows a principal plane cut of the $v_\varphi(\mathbf{n})$ surfaces of cubic austenite of Ni-Mn-Ga, using the room temperature elastic constants of the nearly stoichiometric alloy [8]. The qT2 surface of austenite has pronounced minima for $\mathbf{n}$ pointing in the $\langle 110\rangle_P$ directions, where the subscript P denotes the parent (austenite) phase. The corresponding minimal phase velocity is

$$v_\varphi = \sqrt{c'/\rho}, \quad (2)$$

where $c' = (c_{11} - c_{12})/2 = 3.9$ GPa. These minima correspond to $[1\bar{1}0]_P(110)_P$ shears (i.e. the Bain path shears), along which the high-temperature phase loses its stability. For the NM martensite, the cut of the qT2 surface by the $(010)_M$ plane also exhibits a minimum for a direction close to $[101]_M$ denoted by c'_M in Fig. 1(a). Surprisingly, this direction is not exactly parallel to the lattice vector $[101]_M$, instead, it contains nearly exactly the $\pi/4$ angle with the principal axes, so it can be written as $[1/a\ 0\ 1/c]_M$ or $[c/a\ 0\ 1]_M$ in the lattice direction notation. However, the qT2 surface in fact has a saddle point for this direction; the real global minimum of this surface appears for a direction close to lattice direction $[1/a\ 1/a\ \sqrt{2}/c]_M$ (i.e. $[c/a\ c/a\ \sqrt{2}]_M$). This direction is denoted by c''_M in the $(110)_M$ cut in Fig. 1(c) and again it is inclined exactly by $\pi/4$ from the tetragonal axis. By using equations analogous to Eq. (2), one can calculate elastic moduli for these significant points of the qT2 surface as

$$c'_M = \rho\left(v_\varphi^{[1/a\,0\,1/c]_M}\right)^2 = 25.0\ \text{GPa} \quad (3)$$

and

$$c''_M = \rho\left(v_\varphi^{[1/a\,1/a\,\sqrt{2}/c]_M}\right)^2 = 20.3\ \text{GPa}. \quad (4)$$

These values are higher than the c' modulus for the austenite phase indicating that the elastic anisotropy due to soft shearing modes is much

Table 1
Tetragonal elastic constants of NM Ni-Mn-Ga martensite; experimental results are compared with theoretical predictions by ab-initio methods. The experimental errors were calculated via the sensitivity analysis procedure described in [21].

	c_{11} [GPa]	c_{12} [GPa]	c_{13} [GPa]	c_{33} [GPa]	c_{44} [GPa]	c_{66} [GPa]
Experimental (this work)	197.8 ± 2.3	60.9 ± 3.5	143.5 ± 2.0	189.1 ± 2.9	106.2 ± 1.5	49.7 ± 1.8
Ab-initio [16]	252	74	144	194	100	55
Ab-initio [17]	249	71	141	193	101	56
Ab-initio [18]	250.4	68.0	146.6	193.0	96.5	37.3