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Incommensurateness in nanotwinning models of modulated martensites

Barbora Benešová,[1] Miroslav Frost,[2] Malte Kampschulte,[3] Christof Melcher,[3] Petr Sedlák,[2,*] and Hanuš Seiner[2]
[1]*Department of Mathematics, Julius-Maxmilians University Würzburg, Emil-Fischer-Straße 40, D-97074 Würzburg, Germany*
[2]*Institute of Thermomechanics, Academy of Sciences of the Czech Republic, Dolejškova 5, 182 00 Prague 8, Czech Republic*
[3]*Department of Mathematics I, RWTH Aachen, Pontdriesch 14-16, D-52056 Aachen, Germany*
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We study the formation of modulated martensites in ferromagnetic shape memory alloys by a mathematical model originating from the nanotwinning concept. The results show that the incommensurateness, systematically observed in experiments for the modulated phases, may be understood as a precursor effect of the intermartensitic transitions, and its appearance does not contradict the nanotwinning concept itself. The model sufficiently explains the different levels of incommensurateness reported from different experimental observations for the 14-layered and 10-layered martensites of the Ni-Mn-Ga alloy and outlines the mechanism of formation of faults in the stacking sequences of these materials.

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Low-temperature phases of many ferroic materials tend to form so-called modulated phases, i.e., phases with small periodic disturbances of the atomic positions in the crystal lattice [1–3]. The wavelength of the modulation is typically of the order of few ($\lesssim 20$) interatomic spacings and is always aligned with some principal lattice vector, which enables the construction of a supercell of the modulated structure.

Among the modulated phases, the modulated martensites of ferromagnetic shape memory alloys, and of Ni-Mn-Ga in particular [4–6], have been the most intensively discussed ones recently. In these materials the lattice can exhibit modulations with several different wavelengths (for example, a 10-layer as well as a 14-layer modulation in off-stoichiometric Ni-Mn-Ga) and also a nonmodulated tetragonal phase; as a result, these materials can undergo a sequence of intermartensitic transitions [6–9], i.e., transitions between differently modulated structures or between the modulated and nonmodulated (tetragonal) phases.

The simplest theoretical models explaining the formation and structure of the modulated phases are the *nanotwinning models* [10,11], originating from the concept of adaptive martensite [12]. In these models the modulated phases are interpreted as extremely fine first-order laminates of different variants of the nonmodulated martensite. The nanotwinning models give very good predictions of the effective lattice parameters of the modulated supercells and can also qualitatively explain several effects observed in ferromagnetic shape memory alloys such as the coexistence of 14-layer modulated and nonmodulated structures in Ni-Mn-Ga epitaxial films [11]. The nanotwinning character of the modulations was also confirmed by HRTEM observations [5]. However, the atomic positions of the modulated phases determined by x-ray and neutron diffraction measurements [13–17] systematically deviate from the predictions of these models, showing that the modulation function is rather smooth, not following the zigzag pattern expectable for a first-order laminate with atomistically sharp interfaces. Even more importantly, these measurements confirm that the modulations in many cases are *incommensurate*, i.e., that the periodicity of the modulation function does not exactly fit the periodicity of the superlattice, which cannot be expected from first-order laminates either. These deviations from the nanotwinning model can be partially explained by the presence of stacking faults [11,18] (imperfections of the stacking sequence in the laminates) that affect the averaged diffraction patterns, however, the nanotwinning models cannot offer any explanation why such defects should massively appear in the modulated structure. Moreover, as shown by Li *et al.* [19], the smooth incommensurate modulations lead to smaller misfits at the twinning planes between two different variants of modulated martensites, which also disfavors the nanotwinning concept. For these reasons, many authors interpret the modulations rather as results of band Jahn-Teller effect [20,21] and Fermi surface nesting [22].

In this paper, we show that the experimentally observed smooth and incommensurate modulation functions are not in contradiction with the nanotwinning models; on the contrary, we show that some level of incommensurateness directly results from these models.

Nanotwinning models explain the existence and structure of the modulated phases based on the classical mathematical theory of martensitic microstructures. In this theory, the deformed configurations of the crystal $y(\Omega)$, where Ω is the reference configuration, are expected to be minimizers of energy:

$$E[y] = \int_\Omega W(Dy)\mathrm{d}x + \int_\Omega \varepsilon |D^2 y|^2 \mathrm{d}x, \qquad (1)$$

where the first term is the bulk energy, depending on the deformation gradient Dy, and the second term represents the energetic penalty for the interfaces. The bulk energy is typically *multiwell*, with the individual minima representing the individual variants of martensite. Such a multiwell energy has been routinely used following the pioneering works [23,24], see, e.g., Refs. [25,26]. The form of the surface energy is motivated by the standard choice in phase-field modeling and is used in the context of shape-memory alloys in, e.g., Refs. [25,27]; a strongly related form is found in Refs. [28,29] that predict branching of martensitic laminates. The parameter ε in the surface energy term then determines how fine the resulting laminates can be for prescribed boundary conditions.

*Corresponding author: psedlak@it.cas.cz

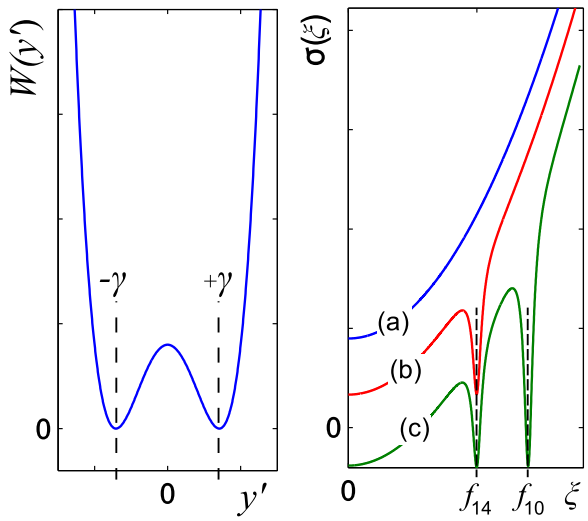

FIG. 1. (Color online) The multiwell characters of the bulk energy (on the left) and the Fourier multiplier $\sigma(\xi)$ (on the right): (a) a standard (quadratic) multiplier; (b) a multiplier favoring 14-layer modulation; (c) a multiplier favoring 14-layer and 10-layer modulations. The curves (a), (b), and (c) are vertically shifted for vividness.

For simplicity and vividness, we restrict the modeling setup in this paper to one dimension (1D) and to *symmetric* modulations: we assume that the modulation function $y = y(x)$, giving the displacements of the atoms in the direction perpendicular to the modulation direction x, oscillates around some fixed, finite mean value, for example $\langle y\rangle = 0$. For Ni-Mn-Ga and other ferromagnetic shape memory alloys, the real stacking sequences are typically *asymmetric*, such as $(3\bar{2})_2$ for 10M martensite and $(5\bar{2})_2$ for 14M martensite, which results in the monoclinic symmetry class of the modulated phase; however, such effects cannot be sufficiently captured in 1D, and so we assume existence of symmetric stacking sequences such as $(5\bar{5})$ [30].

For this particular case where y represents the modulation function in a nanotwinning model on a periodic reference domain $\Omega \subset \mathbb{R}$ of length l, the minima of $W = W(y')$ correspond to the deformation gradients representing the two possible variants of nonmodulated martensite; let us denote these deformation gradients as $\pm\gamma$ (Fig. 1). For the surface energy term, the extremely fine oscillations necessary for describing the modulations may indicate that $\varepsilon \to 0$. However, such a limit does not sufficiently represent the observed tendency to form stacking sequences with the given periodicity and long-range ordering. As seen from the Fourier transform of this term,

$$\int_\Omega \varepsilon |y''|^2 \mathrm{d}x = \varepsilon \int_{\mathbb{R}} |\xi|^2 |\widehat{y'}(\xi)|^2 \mathrm{d}\xi, \qquad (2)$$

where ξ is the frequency vector, $\mathrm{d}\xi = \sum_{k\in\mathbb{Z}} \delta(\xi - 2\pi k/l)$ is the Dirac comb, and $\widehat{y'}(\xi)$ is the Fourier transform of y', the surface energy is minimized when the dominant components of the spatial frequency of the interfaces corresponds to the minimum of the Fourier multiplier $|\xi|^2$. This minimum is attained for zero frequencies, i.e., no interfaces at all. To mimic the spontaneous formation of the modulations we introduce a more general Fourier multiplier $\sigma(\xi) = \sigma(|\xi|)$ that has wells in the frequencies of oscillation observed in modulated structures and otherwise growths quadratically. In the right part of Fig. 1, the possible forms of such multiplier are sketched: (a) the original multiplier $\sigma(\xi) = |\xi|^2$; (b) the multiplier for materials with spontaneous formation of one modulated phase; and (c) a multiwell multiplier for materials able to undergo an intermartensitic transition between two different types of modulations. Without loss of generality, we choose these two minima as corresponding to 14-layer modulations (frequency f_{14}) and 10-layer modulations (frequency f_{10}), $f_{10}/f_{14} = 7/5$.

The resulting model combines some aspects of both the nanotwinning concept (the modulated phase arises as a laminate of individual nonmodulated building blocks) and the electronic-structure based approaches (spontaneous symmetry breaking with a preferred frequency). Such a combination has been previously mentioned by Niemann e*t al*. [11], who pointed out that the Fermi surface nesting and Jahn-Teller effect may serve as small initial disturbances of the lattice triggering the formation of the nanolaminate.

Despite the fact that the modulations occur on the atomistic scale, the model is formulated within continuum mechanics. This is justified by the fact that we aim to model a representative structure that can be understood as the best fitting average over a large number of samples. In this way, we mimic common experimental tools for determining the structure of the modulated phase like x-ray diffraction.

Let us first discuss in detail the case (b) in Fig. 1, i.e., the effect of one additional minimum on the multiplier function $\sigma(\xi)$ onto the energy minimizers. The total energy reads

$$E[y] = \frac{1}{A}\int_\Omega W(y')\mathrm{d}x + A\int_{\mathbb{R}} \sigma(\xi)|\widehat{y'}(\xi)|^2 \mathrm{d}\xi, \qquad (3)$$

where A is a weighting factor of the interfacial energy [31]. If the interfacial term dominates the energy (i.e., $A \to \infty$ in the sense of a Γ limit), minimizers of E are sine waves with a frequency determined by the wells of σ and with prescribed symmetry; recall here that the Fourier transform of a sine-wave is a Dirac delta located in its frequency. In contrast, if the bulk term dominates (i.e. for the Γ-limit $A \to 0$), minimizers correspond to triangle waves. Recall that the spectrum of a triangle wave is a collection of Dirac delta functions, with the highest contribution in a dominant frequency f and then with decreasing weights in the higher harmonics $3f, 5f, 7f$, etc.

In Fig. 2, the behavior in the Γ limits is compared to the case when both bulk and interfacial energies play a role ($A \sim 1$), for which the minimizer was found numerically. This minimizer roughly corresponds to triangle waves with a truncated spectrum because of quadratic growth of interfacial energy, which leads to "blurring" of laminate interfaces. Let us mention that the blurring is necessarily stronger for higher dominant frequencies (i.e., stronger for f_{10} than for f_{14} in our case), as the higher harmonics for higher frequencies are energetically more expensive due to the quadratic character of the function $\sigma(\xi)$ for $|\xi| \to \infty$. From the heuristics point of view, this finding is in agreement with the experimental observations for Ni-Mn-Ga, where much smoother modulation functions are observed for the 10-layered martensite than for the 14-layered martensite. However, for any choice of A, the energy minimizers are perfectly commensurate.

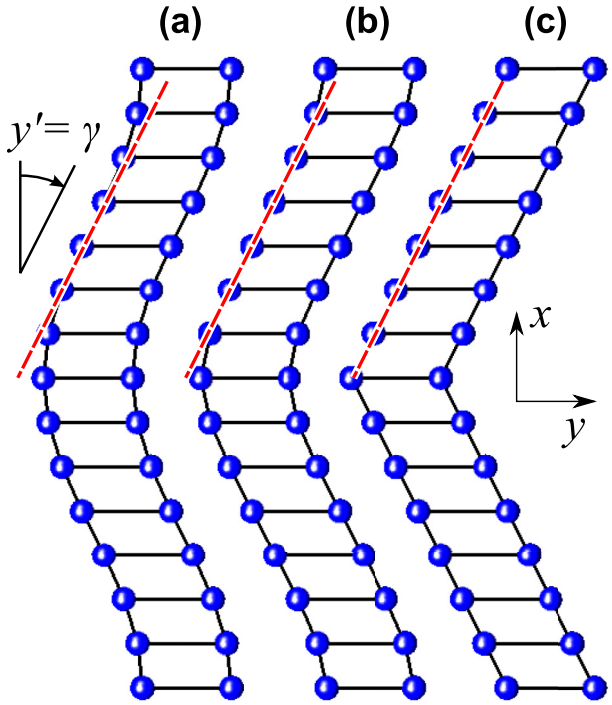

FIG. 2. (Color online) Visualizations of effective modulated unit cells corresponding to energy minimizers for $A \to \infty$ (a), $A \sim 1$ (b), and $A \to 0$ (c). The dashed line denotes the deformation y' corresponding to one of the minima of the bulk energy.

A more complicated situation arises in the case shown in Fig. 1(c), when the minima corresponding to both a 10-layer as well as 14-layer modulations are present. As known from the significant hysteresis for the 10-layer ↔ 14-layer intermartensitic transitions observed experimentally in Ni-Mn-Ga, there may exist relatively broad temperature intervals in which such coexistence of two minima is possible. For example, Khovailo *et al.* [22] observed an austenite → 10-layered martensite → 14-layered martensite sequence upon cooling, but a direct 14-layered martensite → austenite transition upon heating in a $Ni_{2.16}Mn_{0.84}Ga$ alloy, which indicates that the temperature interval of stability the 10-layered phase is completely overlapped by the stability interval of the 14-layered phase.

In this case, we do not attempt to model the intermartensitic transition itself (which would involve the discussion of the localization effects and compatibility between phases, both not treatable in our periodic 1D setting). Nevertheless, the proposed model enables a discussion of the effect of the presence of the second minimum onto the (local) energy minimizers. Figure 3(a) shows the evolution of the energy minimizing modulation function of a 14-layered martensite with the increasing depth of the minimum located at f_{10} for $A \sim 1$. The numerical calculations were performed on a domain of length equivalent to 70 interatomic spacings with periodic boundary conditions; the maximal frequency allowed in the calculation was f_2 to avoid aliasing effects. Figure 3(a) covers one half of this domain, the solution in the second half was identical but mirror-reversed about the x axis. The first calculation was done for only one minimum (at f_{14}) on the $\sigma(|\xi|)$ function; subsequently, the additional minimum was placed at f_{10} and its depth was gradually increased without altering the depth of the f_{14} minimum. It is seen that resulting modulation function evolves from perfectly 14-layer periodic commensurate case into incommensurate, with the positions of maxima and minima shifting in different directions, the amplitudes decreasing, and the modulation curves getting smoother. In the half of the length of the computational domain (i.e., after 35 atomic spacings), the modulation period again matches the periodicity of the interatomic spacing, but this matching is forced by the finite size of the domain and the assumed periodicity; the tendency to deviate from perfect commensurateness and to attain smoother modulation functions is, however, clearly demonstrated.

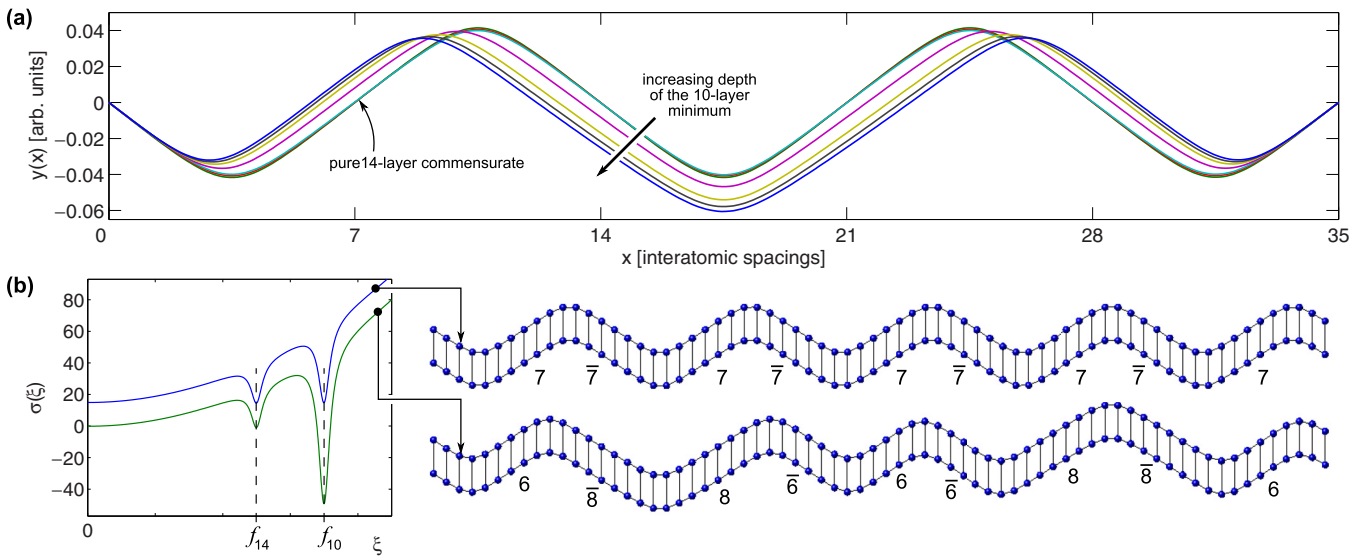

FIG. 3. (Color online) (a) The evolution of the modulation function of the 14-layered martensite with the increasing depth of the f_{10} minimum (one half of the computational domain is shown); (b) visualization of the stacking sequences corresponding to the starting and final depths of the f_{10} minimum.

Figure 3(b) shows a visualization of the effect of the depth of the second minimum onto the modulated structure. If the f_{10} minimum is of a smaller or similar depth as the f_{14} minimum, the structure remains commensurate with a perfectly periodic $(7\bar{7})$ stacking sequence, only the modulation amplitude slightly decreases and the oscillations become smoother. After the second minimum becomes significantly deeper, the stacking sequence becomes strongly faulted; the resulting unit cell can be then only roughly described by a $(6\bar{8})$ sequence. A very similarly faulted stacking was observed also in the experiments: Righi *et al.* [13] reported on a $(4\bar{2}5\bar{2}4\bar{3})$ sequence appearing instead of the perfect $(5\bar{2})_2$ stacking in 14-layered martensite of Mn-rich Ni-Mn-Ga. It is also illustrative to discuss the behavior of this energy minimizer in the $\Gamma-$ limit for $A \to \infty$, where the minimizer converges to a superposition of multiple sine waves with the preferred frequencies, which is similar to the approximations of the modulation functions used in the analysis of x-ray measurements, for example, in Ref. [14].

In summary, the proposed model is able to capture many features of modulated martensites observed experimentally, both these understood as confirming the nanotwinning concepts and those understood as contradicting it. Although the model assumes that the modulated structure is composed of nonmodulated building blocks (i.e., a direct coexistence of NM and 14-layer modulated *via* a branched structure discussed in Ref. [11] is possible), it predicts well the smoothening, incomensurateness, and formation of stacking faults. All these effects are shown here to follow from an additional possible periodicity of the modulations, i.e., from a presence of an additional minimum on the $\sigma(\xi)$ multiplier. If the material tends to undergo an intermartensitic transition, and this second minumum becomes deeper, the level of irregularity increases. Thus the incommensurateness may be be understood as some kind of *precursor effect* for the intermartensitic transition, but may appear also in materials without the intermartensitic transition, as the second minimum could be deep enough to alter the energy minimizing structure, but not sufficiently deep to trigger the transition. The literature data show that the 10-layered and 14-layered martensite in Ni-Mn-Ga can exhibit several different levels of incommensurateness [6,32–34], ranging from perfectly commensurate structures to heavily distorted modulations. This indicates that the commensurateness/incommensurateness is not intrinsic to the modulated structure, but is controlled by some additional external parameter. From the proposed model, we suggest that this external parameter may be the finer structure of the Fourier multiplier.

Nevertheless, the origin of the intermartensitic transitions in FSMAs is not fully resolved yet. As shown, e.g., by Velikokhatnyi and Naumov [35], mainly, the 10-layer modulations in Ni-Mn-Ga may lead to energy reduction *via* the Fermi surface nesting, which is also in agreement with the anomalous increase of electrical resistivity in the 10-layer modulated phase reported by Khovailo *et al.* [22]. The 14-layer modulated martensite can be, on the other hand, stabilized by excess Mn atoms in off-stoichiometric alloys [36]. Simultaneously, the formation of the stacking sequences is probably also affected by the Jahn-Teller effect, which is dominantly responsible for the austenite $\to$ NM transitions [20,37], and thus, may act as a mechanism stabilizing the NM martensite unit cells as the building blocks. Hence, the exact finer structure of the multiplier presumably originates from an interplay of these three phenomena. However, without detailed free energy calculations for the modulated phases, involving also the lattice and magnetic entropy contribution as done for austenite and NM martensite by Buchelnikov *et al.* [38], the multiwell $\sigma(\xi)$ multiplier introduced in this paper has no fully justified physical interpretation so far and must be understood phenomenologically.

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