

Modulated phases in multi-stage structural transformations

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For multistage displacive structural transitions we present a general framework that accounts for various intermediate modulated phases, elastic constant, phonon, and related thermodynamic anomalies. Based on the presence or absence of modulated phases we classify these transformations in four categories and apply this approach to four different representative materials Ni-Mn-Ga (or α -U), NiTi(Fe), Ni-Al, and Cu-Zn-Al. We suggest that the anomalous *increase* in elastic constants and phonon frequency observed when approaching the martensitic transition from above is a signature of the commensurate modulated phase.

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I. INTRODUCTION

A quite varied structural and thermodynamic behavior is observed in a wide class of materials of technological interest such as martensites and shape memory alloys.¹ A displacive structural transition to the low symmetry (“martensite”) phase is often preceded by one or more modulated “phases.”² However, under the vast experimental data, various anomalies and disparate mechanisms, there must be some unifying principles that are common to most of these materials. The present study is an attempt to address this question by identifying and providing a common framework for the different multi-stage transformation mechanisms in displacive martensitic transitions (MT’s). This general framework emerges naturally after appropriately assimilating the existing experimental data. The new *paradigm* being that, concerning structural properties in multistage transformations, very different materials such as magnetic shape memory alloys and actinides (e.g., α -U) exhibit similar behavior which can be understood within a single framework or model. The discussion below is restricted to displacive (nonreconstructive) transitions.

The modulated phase is, in general, an incommensurate phase which, eventually, may lock into a commensurate modulation due to the freezing of a specific phonon, usually with an associated wave vector inside the Brillouin zone. To be more precise, the commensurate modulation may or may not be observed but never without a preceding incommensurate modulation. A general scenario for a cubic symmetry parent (“austenite”) phase is depicted in Fig. 1. Note that, in general, there may be three transition temperatures. (i) T_I is the temperature at which the incommensurate modulation (IC) first appears; this is (presumably) a second order transition. We note that, in real space, this phase is sometimes referred to as “tweed” in the literature. It has been observed in other materials³ such as quartz, high- T_c superconducting perovskites, ferroelectrics, etc. (ii) T_{II} is the temperature at which the commensurate modulation (CM) appears from a (previous) IC phase; this is usually a first order transition. (iii) T_M is the first order MT temperature. Depending on the material, either the commensurate phase or both the commensurate and incommensurate phases may not appear. In the latter case there is no modulation or precursor⁴ phenom-

ena (either in pure or intermetallic crystals) and a direct transition to the martensitic phase takes place.

Concerning the IC phase (“tweed” in real space) we note that in nonstoichiometric alloys there could be *premonitory* effects such as thermal expansion anomalies⁵ that are caused by composition fluctuations⁶ and stabilized by long-range elastic forces.⁷

Based on several experimental observations in a variety of materials we first specify the (likely) *requirements* for a multistage transition.

(a) Existence of low restoring forces along specific directions. In most (cubic) martensitic materials (of interest here) this is accomplished by a temperature softening of the long-wavelength limit of the $[110][1\bar{1}0]$ transverse acoustic (TA_2) phonon branch (i.e., Σ_4 branch). This implies that the shear modulus $C' = (1/2)(C_{11} - C_{12})$ is smaller than the other elastic constants. This effect is related to strain.

(b) Phonon softening (dip) observed in $[110][1\bar{1}0]$ TA_2 branch inside the Brillouin zone usually at a particular value of the wavevector $q \neq 0$. This has an effect on shuffle (i.e., intracell distortion) modes.

Hereafter, we shall take these two requirements as necessary (but not sufficient) conditions for applying the point of view adopted in the present study. Besides, they are observed in most martensitic materials⁸ and accepted to be premonitory indications of the low temperature martensitic phase.⁹ Nevertheless, at the MT, neither the elastic constant nor the phonon soften completely. It is now accepted that an incomplete softening is enough to drive the transition.¹⁰ This is because of an interplay between the strain and the shuffle modes. For onset of the IC, we assume the shuffle mode(s) to be the primary order parameter (OP). Symmetry allowed strain component(s) may then couple to the shuffle as a secondary order parameter, particularly in the CM phase. Depending on the material there may be competition or cooperation between the two effects associated with requirements (a) and (b). In this sense, it is not clear how the interplay between the two partial soft modes operates. In addition, it may be modified by coupling to other physical variables such as magnetism (or inhomogeneities).

This paper is organized as follows. In the next section we provide a new *classification* of martensitic materials in terms

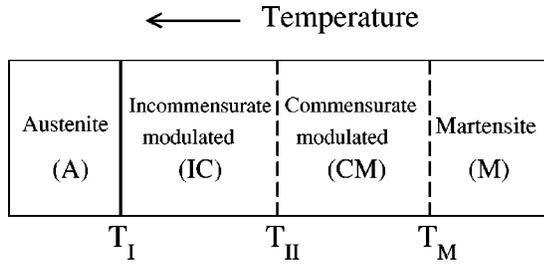


FIG. 1. Paradigm of the multistage displacive structural transitions with modulated precursor phases.

of presence or absence of modulated phases and associated anomalies in phonon dispersion and elastic constants. Section III contains an effective, coupled strain-shuffle, one-dimensional model that explains the observed phonon driven anomalies and modulated phases. In Sec. IV we summarize our main findings and propose new experiments that may validate our predictions.

II. REPRESENTATIVE MATERIALS AND OBSERVED ANOMALIES

According to the general scenario described above, we can broadly classify various displacive martensitic materials in four categories.

(I) Systems that exhibit both, the IC and CM, intermediate transitions. The Ni-Mn-Ga (Refs. 11–14) and α -U (Refs. 15,16) materials belong to this category. Both show anomalies in specific heat,^{16–18} magnetic susceptibilities,¹⁹ resistivity,¹⁶ and an increase in C' with decreasing temperature between T_{II} and T_M .^{15,18,20}

Ni₂MnGa is a ferromagnetic Heusler alloy with cubic symmetry and the magnetism (mainly localized on Mn atoms) arises from d electrons. At low temperatures it transforms (for compositions close to stoichiometry) to a tetragonal martensitic phase.²¹ The phonon anomaly is observed at a wave vector $q = \frac{1}{3}[\xi, \xi, 0]$, where $0 < \xi < 1$.

α -U is an orthorhombic material and displays two IC phases-incommensurate modulation in one direction or in two directions. The origin of magnetism is (likely to be) the highly directional f electrons in actinides (U here). The phonon anomaly is observed at $q = \frac{1}{2}[\xi, 0, 0]$. The martensitic phase is presumably monoclinic but this is not yet known although there is a small peak in specific heat recently observed¹⁶ at 1.2 K.

We notice that for materials in this group, the lock-in transition at T_{II} occurs without a change in symmetry (at least on an average).

(II) In this second category we include those systems, although they exhibit the two modulated phases, in which the lock-in transition is accompanied by a change in symmetry. As a prototype we take the NiTi(Fe) material.^{22–24} This shape memory alloy (SMA) has a high temperature cubic structure and exhibits an IC phase. It also locks into a CM phase with trigonal symmetry (i.e., an intermediate R phase) before going into a monoclinic martensite.²⁵ Very recent high resolution transmission electron microscopy experiments²⁶ in Ni-Ti have confirmed the existence of the IC phase. More

interesting is the observation that the degree of incommensurability decreases with temperature to finally lock into the (CM) R phase. On the other hand, it has been pointed out that the R phase is a legitimate martensite competing with the monoclinic martensite.²⁷ Note that this competing martensitic phases scenario is consistent with our framework. There is a small tendency for C' to have an up-turn with decreasing temperature^{28,29} and the phonon anomaly is observed at $q = \frac{1}{3}[\xi, \xi, 0]$. In this case the freezing of the phonon with decreasing temperature (unlike the case I above) is accompanied even by a change in space group symmetry (from cubic to trigonal) related to the underlying phonon displacement amplitude.²⁷ Note that stoichiometric AuCd (Refs. 25,30) also has a $B2$ to R phase transition similar to NiTi(Fe).

(III) In this category we include systems in which the CM phase is suppressed ($T_{II} = T_M$). This is the case of the Ni_xAl_{1-x} ($0.45 < x < 0.63$) (Refs. 31,32), Fe_{1-x}Pd_x ($x < 0.32$) (Refs. 33,34), Fe₃Pt (ordered) (Ref. 35), and In-Tl (Ref. 36) materials. They exhibit an IC phase (referred to as tweed, in real space) but the CM phase is absent before they undergo a MT. The phonon anomaly in NiAl is observed at $q \approx \frac{1}{6}[\xi, \xi, 0]$ with a monoclinic martensitic phase.

(IV) In the case of Cu-based shape memory alloys (e.g., Cu-Zn-Al), no modulated phase is observed. There is a unique phase transition from the high temperature cubic austenite phase directly to the martensitic phase. In phonon dispersion curves there is almost no dip but significantly, the whole (TA₂) phonon branch has a quite low energy. These materials can be termed as ordinary SMA with entropy driven^{8,37} MT.

We note that materials discussed in the above categories exhibit the same premonitory effects but different structural precursors.⁴ The different transitions are accompanied by anomalies in various physical quantities with different magnitudes.

(i) Softening of a specific *phonon branch* accompanied by a dip. Figure 2 shows experimental examples for Ni-Mn-Ga (Refs. 13,14) α -U (Ref. 38) and Ni-Al (Ref. 32). For the purpose of discussion below, the two cubic alloys Ni-Mn-Ga and Ni-Al are shown together and α -U (orthorhombic) is shown in the inset. Note the appealing *similar* behavior of phonons in Ni-Mn-Ga and α -U. Except for a linear decrease, there is no interesting feature in Ni-Al phonons such as a conspicuous change in slope. The different transitions are denoted by arrows. The increase in energy at low temperature for Ni-Mn-Ga is an indication of the phonon freezing at T_{II} . Presumably the α -U should also exhibit similar low temperature increase in phonon energy but unfortunately the experimental data is lacking.

(ii) Softening of the relevant elastic constants (i.e., the long-wavelength limit of TA₂ phonon branch). An example for C' and C_{44} softening as the temperature is decreased to T_{II} and elastic constant “hardening” upon subsequent cooling^{18,20} to T_M for Ni-Mn-Ga is depicted in Fig. 3(a). In contrast, other than a linear decrease there is no structure in the behavior of elastic constants for Ni-Al, also shown on the same figure for comparison. In Fig. 3(b) we show the temperature variation of three of the relevant orthorhombic elas-

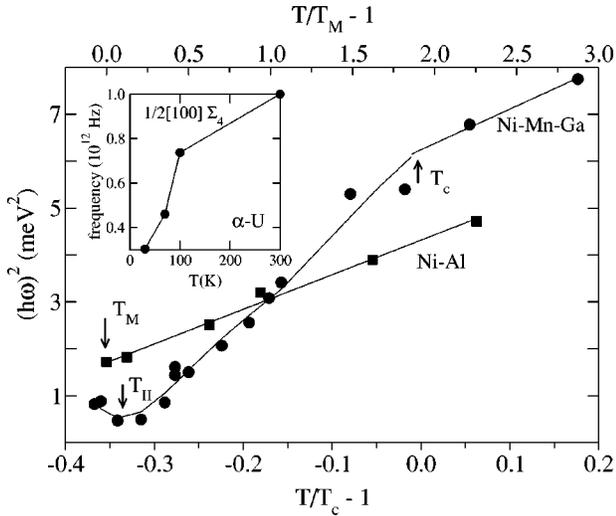


FIG. 2. Energy of the anomalous phonon as a function of reduced temperature for Ni-Al (T_M) and Ni-Mn-Ga (T_c). T_c is the Curie temperature and T_I cannot be properly identified. The inset shows the phonon softening in α -U. Data have been extracted from references indicated in the text.

tic constants for α -U (Ref. 39). There is a striking similarity in the C_{11} and C_{44} variation for α -U and the C' and C_{44} variation for Ni-Mn-Ga (Ref. 40). Unfortunately, the C_{12} low temperature data for α -U is lacking. We also note that a somewhat similar incipient anomaly is observed in NiTi(Fe) (Ref. 41). In this work, we shall argue that the up-turn (or elastic constant “hardening”) with decreasing temperature at T_{II} is characteristic of systems undergoing multistage modulated structural transformations. This point will be discussed below.

(iii) Anomalies in the specific heat, resistivity, magnetic susceptibility and other thermodynamic variables are also observed. Examples include Ni-Mn-Ga (Ref. 8), NiTi(Fe) (Ref. 23), α -U (Ref. 16), and other actinides.⁴²

The IC phase is detected by diffuse satellite reflections that appear at incommensurate positions.⁴³ Examples include Ni-Mn-Ga (Ref. 11), Ni-Al (Ref. 31), Fe-Pd (Ref. 34), NiTi(Fe) (Refs. 26,44). It is not caused by a phonon instability but it is due to local inhomogeneities⁶ (e.g., compositional fluctuations, crystal defects, residual strain) that (locally) couple to the soft modes. The emerging phase is thermodynamically stabilized by anisotropic, long-range elastic forces.⁷ However, this remains an open question for future investigation. The further lock-in (or freezing) of the phonon at commensurate positions requires an *additional* degree of softening of the anomalous phonon frequency with decreasing temperature before it reaches the martensitic transition T_M . It is clear from Fig. 2 that in the case of Ni-Mn-Ga, magnetism provides (through a magnetoelastic coupling⁴⁵) the enhancement of softening necessary for freezing.

Moreover, it is known that in many martensitic alloys the transition temperature T_M is very sensitive to the electron concentration per atom (e/a). This has not been *quantified* previously, but clearly so. In Fig. 4(a) we compare various transition temperatures for three materials:²² NiTi and

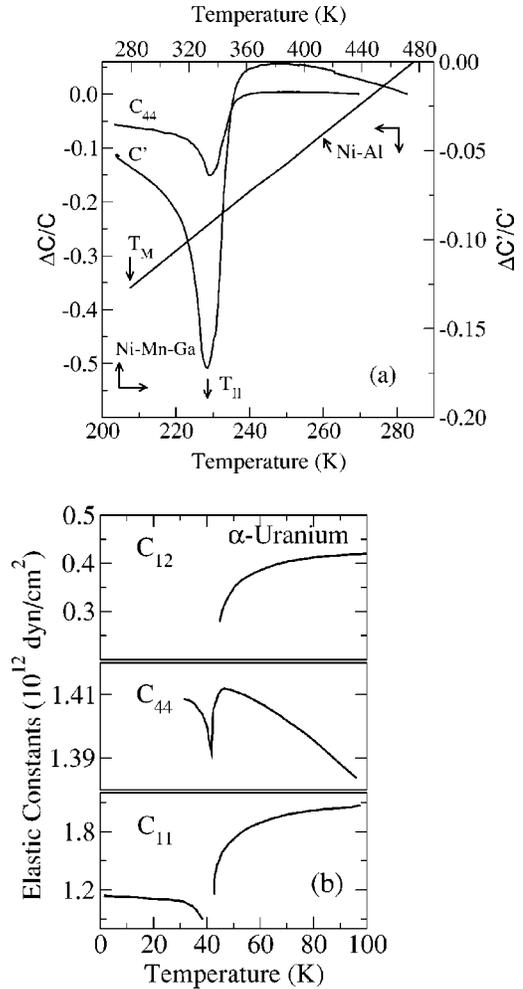


FIG. 3. (a) Elastic constant anomaly in Ni-Mn-Ga compared to that in Ni-Al. (b) Elastic constant anomaly in α -U. Data have been extracted from references indicated in the text.

NiTi(Fe) for two different compositions as a function of e/a . (The stable phase for $T_{II} < T < T_M$ is rhombohedral (R) and modulated.²⁷) This dramatic dependence of lattice stability with the e/a ratio is also observed in Ni-Mn-Ga (Ref. 8) and Fe-Pd (Ref. 46) as well [see Fig. 4(b)]. However, the trend is reversed in Fe-Pd [inset of Fig. 4(b)] because, unlike Ni-Mn-Ga and Ni-Ti, Fe-Pd is a close-packed (magnetic) structure. Small changes in the relative alloying percentages of the elements may produce significant variations in T_M and therefore in the observed behavior of the materials. This is especially relevant in Cu-based alloys and *actinides*, particularly in Ga stabilized⁴² Pu. Beyond a certain alloying percentage, the martensitic transition can be arrested totally (e.g., above^{33,34} 32 % Pd in Fe-Pd). More precisely, as T_M increases, the freezing of the phonon prior to the martensitic transition becomes less likely.

III. EFFECTIVE 1D MODEL

From the full three-dimensional crystal symmetry analysis we have a Ginzburg-Landau model in terms of all (six) strain tensor components,^{47,48} all shuffle²⁴ order parameters, and

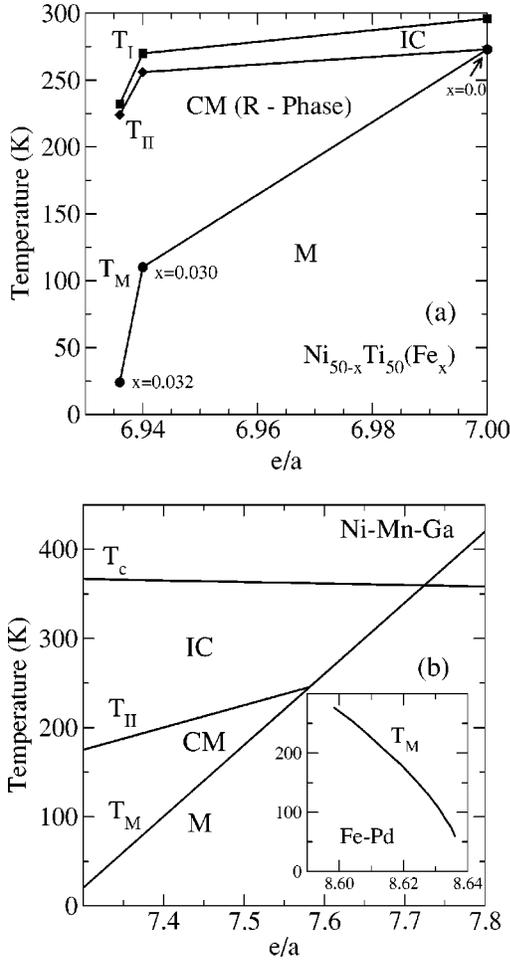


FIG. 4. Various transition temperatures as a function of e/a in (a) Ni-Ti (after Ref. 22), (b) Ni-Mn-Ga (Ref. 8), and in the inset Fe-Pd (Ref. 46).

the magnetization⁴⁷ with the symmetry allowed couplings between strain and shuffle, strain, and magnetization as well as shuffle and magnetization. For specific strain components and the shuffle in a particular direction we can obtain an effective one-dimensional analog of the full 3D model. We emphasize that our goal here is to address the ion-displacive (or phonon-driven⁴⁹) anomalies (above T_M) but not the microstructural aspects (for which we need to include the gradient terms⁵⁰). Therefore, the effective 1D model is especially appropriate for our purpose.

We focus on the $\vec{q}=[\xi\xi 0]$ projection of the cubic \rightarrow tetragonal distortion. The relevant order parameters are the amplitude of the anomalous phonon η and the tetragonal strain e (e_3 in standard symmetry-adapted notation). The simplest Landau free-energy expansion is

$$F(e, \eta) = \frac{\omega^2}{2} \eta^2 + \frac{\beta}{4} \eta^4 + \frac{\gamma}{6} \eta^6 + \frac{C'}{2} e^2 + \frac{A}{3} e^3 + \frac{B}{4} e^4 + \kappa_{e\eta} e \eta^2, \quad (1)$$

where ω is the frequency of the anomalous phonon and C' the elastic constant defined as $C' = (C_{11} - C_{12})/2$. Both

soften with decreasing temperature (for the cubic materials considered here). Here $\kappa_{e\eta}$ is a material dependent parameter denoting symmetry allowed coupling between strain and shuffle.

For the analysis of the modulated phases, we write an effective free-energy in terms of the shuffle η only, i.e.,

$$F_e(\eta) = \frac{\omega^2}{2} \eta^2 + \frac{\beta_r}{4} \eta^4 + \frac{\gamma}{6} \eta^6, \quad (2)$$

with the renormalized coefficient (including fluctuations and anharmonicities¹⁰) being

$$\beta_r = \beta - 2(\kappa_{e\eta})^2/C'. \quad (3)$$

The associated tetragonal distortion is given by⁵¹

$$e = -(\kappa_{e\eta}/C') \eta^2, \quad (4)$$

considering only the harmonic terms in strain.

In the IC phase $\beta_r > 0$ and the last term in the η expansion (2) is not relevant (in addition to the shuffle amplitude being very small). One possible origin of this phase is local inhomogeneities that couple to the soft modes⁶ and renormalize the quadratic coefficient so that in some regions the corresponding renormalized phonon frequency ω_r^2 becomes negative. T_I is the temperature at which anisotropic long-range elastic forces stabilize the IC phase. Then, the intensity of the satellite reflections continuously increases from zero with decreasing temperature and consequently the magnitude of the associated tetragonal strain, which serves as a precursor to martensite.

As the order parameter η increases,^{14,23} the sixth-order term in Eq. (2) becomes important. The lock-in of the phonon at commensurate positions requires that $(\kappa_{e\eta})^2/C'$ be large enough so that $\beta_r < 0$. This is a phonon instability and the transition at T_{II} is first order.

Subsequent cooling is dominated by the increasing phonon amplitude and the softening of C' is not required for the structural instability at T_M . Actually, materials undergoing the lock-in transition (Ni-Mn-Ga, α -U) exhibit a *hardening* of the relevant elastic constant(s) in the range $T_M < T < T_{II}$ (see Fig. 3). We suggest this unusual behavior (when approaching a structural phase transition) is *characteristic* of materials for which the phonon instability occurs *prior* to the structural instability. The *upturn* at T_{II} reflects the higher stability of the CM (averaged cubic) phase with respect to the parent cubic phase. The further structural instability results from a symmetry allowed coupling of strain to the increasing value of η [that is, from Eq. (4), $e = -(\kappa_{e\eta}/C') \eta^2$].

This analysis may be expanded to include secondary couplings.

(i) Effect of softening in C_{44} : Ren and Otsuka⁵² pointed out that in some materials C_{44} also softens with temperature and consequently there may be a competition between both C' and C_{44} modes. In that case,

$$F(e, \epsilon, \eta) = F(e, \eta) + \frac{C_{44}}{2} \epsilon^2 + \kappa_{\epsilon\eta} \epsilon \eta^2, \quad (5)$$

where ϵ is the corresponding (symmetry-adapted shear e_4) strain and $\kappa_{e\eta}$ the strength of the symmetry allowed coupling term. The expression of $F(e, \eta)$ is given by Eq. (1). We may write an effective free-energy in terms of η and obtain that the renormalized coefficient is now given by

$$\beta_r = \beta - \frac{2(\kappa_{e\eta})^2}{C'} \left[1 + \frac{(\kappa_{e\eta}/\kappa_{e\eta})^2}{A} \right], \quad (6)$$

where $A = C_{44}/C'$ is the *elastic anisotropy*. The coupling between both shear modes is then given by

$$\epsilon = \left[\frac{\kappa_{e\eta}}{\kappa_{e\eta}} \right] \frac{e}{A}. \quad (7)$$

We emphasize that this relationship between the two shear strains is naturally mediated through the elastic constant anisotropy (A).

(ii) Role of magnetism: From the existing data, it appears to renormalize the shuffle coefficients (see Fig. 2). Clearly, d electrons are responsible in NiTi(Fe) and Ni-Mn-Ga while f electrons are crucial in α -U and other actinides, especially^{42,53} Pu. The “kink” observed at the Curie point T_c is described by writing $\omega_r^2(m) = \omega^2 + \kappa_m \eta m^2$ (with $\kappa_m \eta < 0$), where m denotes magnetization. Other couplings that renormalize the strain coefficients are also very likely. Unfortunately there is no data on the behavior of C' around T_c .

(iii) For α -U it follows from symmetry analysis that the monoclinic strain is coupled to the frozen phonon amplitude.⁵⁴ Thus, the anomaly at 1.2 K in the specific heat¹⁶ may be an indication of MT to a monoclinic phase. This may also happen for other actinides, including the apparently strange behavior^{42,53} of Pu.

IV. CONCLUSION

We have proposed a general framework for understanding multistage martensitic transformations which is consistent with a large amount of experimental data on different materials such as Ni-Al, Ni-Mn-Ga, NiTi(Fe), α -U, Fe-Pd, Au-Cd, etc. Specifically, presence of an incommensurate, and in some cases an additional commensurate, modulated phase as precursors to the MT reflects itself in the anomalous (softening and further “hardening”) of both the elastic constants

and phonons. In the case of some magnetic martensites, particularly Ni-Mn-Ga, the phonon softening is enhanced by magnetism. We propose additional experiments that may test the broader validity of our scenario. (i) Measurements of C' in Ni-Mn-Ga as a function of temperature with the hope of observing a change in slope around T_c . (ii) Low temperature (below 30 K) measurements of phonon dispersion in α -U to observe a possible up-turn (akin to that in Ni-Mn-Ga). (iii) Measurements indicating a possible structural phase transition to a monoclinic martensite around 1.2 K in α -U and possibly a similar transition in α -Pu below 60 K.

From the new perspective presented here it is clear that, concerning structural behavior, the underlying physics in such disparate systems as shape memory alloys and certain actinides is quite similar. We have attempted to extract some unifying principles that provide new insight into multistage, modulated structural transformations. Moreover, these connections may enable exchange of concepts and expertise from one set of materials to another and vice versa.

Inclusion of fully three-dimensional strain, shuffle and magnetization gradient terms⁵⁰ will allow us to study domain walls, especially antiphase boundaries, twin boundaries and microstructure by augmenting the Landau free energy with Ginzburg terms⁴⁸ in multistage transformations. It remains to be explored how the multistage character of the transformation affects domain wall orientation and energetics, specifically the microstructure.

This global view of the many factors implicated for different materials has drawn our attention particularly to the need for further study, in any complex material, for new, refined measurements of heat capacities and magnetic susceptibility.

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