Spin-Glass Nature of Tweed Precursors in Martensitic Transformations

Sivan Kartha, Teresa Castán,[a] James A. Krumhansl,[b] and James P. Sethna
Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York 14853-2501
(Received 19 June 1991)

Many displacive solid-solid transformations, despite being first order, show pronounced precursor effects, such as the mesoscopic, micron-scale, "tweed" pattern seen in shape-memory alloys. We model this tweed theoretically using a nonlinear, nonlocal elastic free energy, and argue that quenched concentration inhomogeneities drive the local tweed modulations. We report (1) the construction of a model for $\{11\}/\langle 1\bar{1}\rangle$ shear transformations in square systems, (2) a simulation including concentration inhomogeneities, and (3) a mapping of the disordered 2D martensite onto an infinite-range spin model, identifying tweed with the spin-glass phase.

PACS numbers: 81.30.Kf, 61.70.Wp, 75.10.Nr

In textbook first-order phase transitions critical fluctuations are negligible: Water shows no hint of incipient solidity above 0 °C. First-order solid-solid displacive transformations are strikingly different; precursors are common for tens through hundreds of degrees away from the transitions. We study here the tweed pattern [1] observed in electron micrographs well above the transition temperature in the so-called medium and weak martensites, including the shape-memory alloys FePd [2] and NiAl [3], the superconducting A-15's [4], and high-T_c Y-Ba-Cu-Co-O, and Y-Ba-Cu-Al-O [5,6]. The tweed appears as a characteristic cross-hatched pattern. X-ray- and electron-diffraction measurements [2,3,7–10] indicate that tweed is a local mixture of undeformed and deformed regions, and that it arises from a local $\{110\}/\langle 1\bar{1}0\rangle$ shear [1,3].

This paper considers the two-dimensional square to rectangular transition as a simple model for the three-dimensional cubic to tetragonal transition in metallic systems. Near the transition, these materials show a marked softening [11] of the elastic constant $C'=(C_{11}-C_{12})/2$ [the resistance to rectangular (deviatoric) shears], and have large elastic anisotropy [12]; hence C_{44}/C' and $(C_{11}+2C_{12})/C'$ are both large. We thus consider the formal limit where this elastic anisotropy is infinite; i.e., the *only* allowed deformations are rotations, translations, and volume-preserving rectangular stretches (deviatoric strain). We subsequently relax these constraints.

Our theoretical model formally supports the proposal that the existence of some disorder is of central importance in the tweed precursor [13]. Suggestively, in pure zirconium and titanium, central-peak precursors do not appear above the ω phase transition, but do appear in samples alloyed with as little as 1% oxygen or nitrogen [14]. We are further motivated by the drastic dependence of the martensitic transition temperature on concentration. For example, in $Fe_{1-\eta_0}Pd_{\eta_0}$ [2], the martensitic transformation temperature changes from 0 to 300 K as the concentration η_0 varies from 32% to 29%. Within a local region in any alloy, the local concentration $\eta(x,y)$ will exhibit static, quenched-in, statistical variation about the nominal concentration η_0; we consider the proposal that these inhomogeneities drive the local deformations in the material, forming tweed.

Our order parameter is the component of the strain tensor corresponding to local rectangular deformation, $\phi\equiv e_{xx}-e_{yy}$. As mentioned above, the materials of interest have substantial softening of C' and consequently large elastic anisotropy. We begin with the ansatz that only deformations composed of $\{11\}/\langle 1\bar{1}\rangle$ shears are important. In this limit (infinite elastic anisotropy) the strain field has (1) no bulk dilation ($e_{xx}+e_{yy}=0$) and (2) no diagonal shear (i.e., $\{10\}/\langle 01\rangle$, hence $e_{xy}+e_{yx}=0$).

These constraints result in a strain field which is simply a superposition of one-dimensional modulations along the $\langle 11\rangle$ directions [15]. Denote the Cartesian displacement field by $\mathbf{U}(x,y)=(X(x,y),Y(x,y))$ and change the variables to $i=x+y$ and $j=x-y$. Applying constraints (1) and (2), we obtain $(X+Y)_i=(X-Y)_j=0$ and thus $X+Y$ is a function of j only, while $X-Y$ is a function of i only. Thus, most generally,

$$\mathbf{U}(x,y)=\begin{pmatrix}1\\-1\end{pmatrix}U_+(x+y)+\begin{pmatrix}1\\1\end{pmatrix}U_-(x-y)\,, \qquad (1)$$

and consequently $\phi(x,y)\equiv e_{xx}-e_{yy}=\phi_+(i)+\phi_-(j)$; two orthogonal modulations completely describe the displacement and strain fields.

Superpositions of diagonal modulations of this type are present in the simulations of Khachaturyan [16]. If the modulations occurred in only one direction, we could think of them as a lattice of solitons or twin boundaries: The period-on theories [17] and the subsequent dressed embryo theories [18] of tweed are based on this idea. The transparent decomposition we introduce above in the limit of infinite anisotropy gives an aesthetically appealing explanation for tweed, and allows for further analytical and numerical progress, below.

Imposing this constraint, we use standard group-theoretic methods to arrive at the following expression for the Landau-Ginzburg free energy [9,17,19] for the two-dimensional square to rectangular transition. To sixth order in ϕ and second order in gradients, the most general free energy can be rescaled into the form

$$f(\phi)=\{\alpha_T(T-T_0)+\alpha_\eta[\eta(x,y)-\eta_0]\}\phi^2 -\phi^4+\phi^6+\kappa_1(\nabla\phi)^2+\kappa_2(\partial_x^2\eta-\partial_y^2\eta)\phi\,. \qquad (2)$$

Note that the quadratic term $\alpha(x,y)$ embodies the sensitive dependence of the transition temperature on the local concentration $\eta(x,y)$. When κ_2 and α_η are zero this free energy reduces to the standard triple-well potential for a first-order transition. There is also a term allowed by symmetry which couples $\partial_x^2\eta-\partial_y^2\eta$ linearly to the order parameter ϕ; it exemplifies the physics discussed by Robertson and Wayman [3] and simulated by Clapp [20], who emphasize how substitutional disorder introduces local atomic displacements which, when they break the cubic symmetry, can push the system into one of the tetragonal variants.

We now introduce the central physical assumption that the transition is driven by *static* (quenched) concentration inhomogeneities. Observations of martensitic tweed [1,2,4] show the patterns to be constant with time and largely reproducible with temperature cycling. Diffusion might drive precursors in some systems as suggested by Khachaturyan [16] and Marais *et al.* [21], where defects are known to be highly mobile, but we do not believe this to be generally the case in martensites. Another consideration is whether the patterns are simply the result of small, elastic distortions driven by the defect distribution, as in Robertson and Wayman [3] and Jiang *et al.* [6]; again there is uncertainty depending on specific circumstances. The issue is whether the distortions are smaller than or comparable to the transformation deformation; the evidence [1,2,4] suggests the latter in the cases we consider.

We now have all the necessary ingredients. The local first-order transformation temperature $T_M(x,y)$ depends linearly on the local concentration $\eta(x,y)$ according to $T_M(x,y)=T_M(\eta_0)-(\alpha_\eta/\alpha_T)[\eta(x,y)-\eta_0]$. Therefore, the local transformation temperature will lie above the experimental laboratory temperature T in some regions of the sample, and in other regions, below. For example, if α_η is positive, as in FePd [2], the system will try to form local martensitic regions where the palladium concentration is low and will remain cubic where it is high.

We use standard Monte Carlo techniques to investigate the resulting modulation of the order parameter $\phi(x,y)$ as the simulated system attempts to accommodate the disorder by locally fluctuating between the high- and low-temperature phases. At each point (x,y) of an $N\times N$ lattice the order parameter is a superposition of contributions from each one-dimensional diagonal modulation, so $\phi(x,y)=\phi_+(i)+\phi_-(j)$. Concentration inhomogeneity is introduced by giving $\alpha(x,y)$ a Gaussian distribution with a temperature-dependent mean, and a width determined by the strength of the coupling between concentration and ϕ.

Figure 1 shows a structure obtained after performing the minimization in the tweed regime. Notice that while long-range diagonal order is imposed by our constraints, the fact that the ground state actually does modulate in both directions is reassuring. We vary the effective temperature by changing the average quadratic term: As we cool, we go from a square phase, through a temperature range of tweed, to a low-temperature twinned martensite phase. The tweed to martensite transition appears first order and has substantial hysteresis: The modulation wavelength in the martensite and the amount of hysteresis are nonequilibrium effects and will depend on the thermal history and the Monte Carlo dynamics. A natural feature of these two-dimensional tweed solutions is that ϕ_+ modulates between austenite (A) and one of the martensitic variants (say, $+M$) while ϕ_- modulates between (A) and the *other* variant ($-M$). Any other possibility is energetically very improbable.

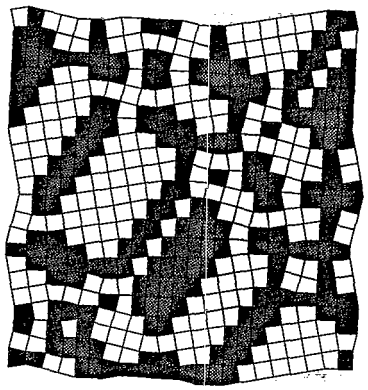

FIG. 1. Theoretical tweed. Strained two-dimensional lattice, found by minimizing the elastic free energy for a disordered martensite. The grey regions are mixed between the two rectangular martensitic variants; the white is square austenite. The temperature is in the middle of the tweed regime, where the transition from austenite (square) to martensite (rectangular) would occur in the absence of disorder. We have chosen the value of the gradient term $\bar{\kappa}=0.003$ to make the thickness of the distinct rectangular regions (the correlation length ξ) aesthetically pleasing. The constant $\kappa_2=0$, and $\delta t=0.05$. On different quenches with the same disorder we find many qualitatively similar metastable states.

In the case of $\kappa_1=0$, there is no need for gradual phase boundaries between austenitic and martensitic regions of the system, and the order parameter can then abruptly shift from one phase to the other. This feature lends to the two-dimensional problem a natural description in terms of spinlike variables; a simpler model is discussed by Fuchizaki and co-workers [18]. We map $\{\phi_+(i)\}$ to a set of N spins $\{s(i)\}$ such that $s(i)=1$ or -1 corresponds to $\phi_+(i)=M$ or A. Similarly, we map $\{\phi_-(j)\}$ to a set of N spins $\{\sigma(j)\}$ such that $\sigma(j)=1$ or -1 corresponds to $\phi_-(j)=A$ or $-M$. If $s(i=x+y)$ and $\sigma(j=x-y)$ are parallel, the site (x,y) is martensite, $\phi(x,y)=\pm M$; if antiparallel, the site is austenite, $\phi(x,y)=0$. Thus the concentration $\eta(x,y)$ maps onto a random bond J_{ij}. Similarly, the $(\partial_x^2\eta-\partial_y^2\eta)\phi$ term in Eq. (2) contributes to a random field h_i on $s(i)$ and f_j on $\sigma(j)$. An applied stress will also add terms linear in $s(i)$ and $\sigma(j)$.

In the infinite anisotropy limit, with zero gradient energy ($\kappa_1=0$), the martensitic free energy of a two-dimensional [22] lattice is the random-field version [23] of

the antiferromagnetic [24] Sherrington-Kirkpatrick model [25],

$$\mathcal{H}=\sum_{i=1}^{N}\sum_{j=1}^{N}J_{ij}s_i\sigma_j+\sum_{i=1}^{N}h_is_i+\sum_{j=1}^{N}f_j\sigma_j\,. \tag{3}$$

The interactions $\{J_{ij}\}$ are independent random variables with a Gaussian probability distribution of mean J_0 and width J. Motivated by simplicity, we concentrate on the random-bond model, by taking the coupling with the disorder through the coefficient $a(x,y)$ only, and assuming $\kappa_2=0$, whence the random fields $h_i=f_j=0$.

Note that $J_0(T)$ effectively corresponds to the free-energy difference between the martensite and austenite phases at the nominal alloy concentration η_0, and J corresponds to the change in J_0 with concentration at a given temperature. Thus, at high temperatures, $J_0(T)>J$ and the system will have a square, antiferromagnetic, austenitic ground state, and at low temperatures, $-J_0(T)>J$ and the system will have a rectangular, ferromagnetic, martensitic ground state. In between, $|J_0(T)|\leq J$, the disorder leads to a random, spin-glass tweed phase. The phase diagram [24] is shown in Fig. 2.

We can estimate the expected range of tweed for FePd by using the concentration dependence of the transition temperature and the random variations in the local concentration. Ignoring chemical clustering effects, the inhomogeneity due to statistical variations in the local concentration is $\Delta\eta\sim[\eta_0(1-\eta_0)/n]^{1/2}$, where n is the number of particles in a strain-correlated region. Typically, n is a few hundred particles [8,26], say, $n\sim400$. We use the experimental value [27] $\partial T_M/\partial\eta_0\sim-10^4$ K for FePd (300 K for a 3% shift in concentration). Thus, the local transition-temperature fluctuations, and thus the predicted tweed regime, would extend in Fe–30% Pd for ~450 K. Experimentally, tweed contrast in Fe–30% Pd is observed over a range of nearly 100 K above the martensite start temperature [28]. Many effects (like the gradient term κ_1) ignored in our phase diagram can suppress the tweed modulations. It is clear, though, that concentration inhomogeneity provides plenty of driving force for tweed.

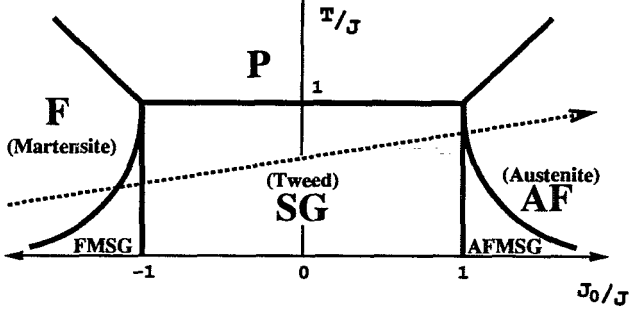

FIG. 2. The phase diagram expected (see Ref. [30]) for the antiferromagnetic spin glass, Eq. (3). A given sample at a fixed nominal concentration η_0 will trace a sloped path as temperature is decreased (dashed line). The paramagnetic phase, which would have tweed modulations driven by thermal fluctuations, is presumably preempted by another phase (e.g., the melt). The two magnetized spin-glass phases [ferromagnetic (FMSG) and antiferromagnetic (AFMSG)] will be discussed in a later publication.

The constraints of no bulk dilation or diagonal shear have provided a clear, intuitive explanation for the tweed morphology. What happens as we relax these constraints? The infinite-range strain-strain correlations will now decay over a distance L along the $\langle11\rangle$ directions, and over a distance ξ along the $\langle10\rangle$ directions, where ξ is the thickness of a correlated rectangular region within the tweed structure. We can estimate L and ξ by balancing the dominant energies in the problem.

The first of the important energy scales is the energy gained by the coupling to the nonuniform concentration field $\eta(x,y)$. There is one degree of freedom in each correlated region of area $\sim L\xi$. In this area, the statistical variation in the concentration will scale as the inverse square root of particle number: $\Delta\eta=a[\eta_0(1-\eta_0)/L\xi]^{1/2}$, where a is the lattice constant. Since the concentration field couples with a strength α_η, the energy density gained from the coupling to concentration is $E_{\rm conc}\sim-\alpha_\eta\phi_0^2a[\eta_0(1-\eta_0)/L\xi]^{1/2}$, where ϕ_0 is the martensitic strain.

The second important energy scale is the bulk dilation and diagonal shear energy needed to accommodate the violation of the elastic constraints. We find that the bulk dilation and diagonal shear energy $B(e_{xx}+e_{yy})^2+D(e_{xy})^2$ needed to weave our domains together scales as $E_{\rm weave}\sim(B+D)\phi_0^2(\xi/L)^2$. Balancing these two energies leads to the tweed domain-size estimate [29] $L\sim\xi^{5/3}/(\epsilon a)^{2/3}$. Here $\epsilon=\alpha_\eta[\eta_0(1-\eta_0)]^{1/2}/(B+D)$ is a small parameter [27] reflecting the relative strength of the concentration inhomogeneity and the bulk modulus, which gives us $L\gg\xi$. The final important energy scale is the gradient energy which resists order-parameter variations: $E_{\rm gradient}=\kappa_1(\phi_0/\xi)^2$. Introducing this energy into the discussion determines $\xi\sim[\kappa_1/(B+D)]^{3/2}(\epsilon a)^{-2}$.

What experimental consequences are suggested by this analogy to spin glasses? In magnetic spin glasses, the two most distinctive behaviors are the *nonlinear* magnetic susceptibility and the "glassy dynamics." Here the equivalent would be anomalies in the *nonlinear* elastic constants, as the tweed range is entered, and path dependence (hysteresis) leading to the possibility of different mesostructures arising from cooling in an applied stress then removing it, versus simply cooling without stress. We are not yet in a position to make any detailed predictions.

We believe, however, that the limiting model developed here, infinite elastic anisotropy, with discretization of displacement fields in a pseudospin representation, driven by concentration inhomogeneities (intrinsic to alloys), contains the essential general physics needed to understand ubiquitous mesoscopic precursor patterns observed over wide temperature ranges in many martensitic transformations. Many of the tweed-forming martensites are tech-

nologically important, and the spin-glass viewpoint may suggest studies, particularly on the dynamics of martensitic alloys, that will provide new insights.

We acknowledge the support of DOE Grant No. DE-FG02-88-ER45364. T.C. wishes to thank the Laboratory of Atomic and Solid State Physics for their hospitality, and the DGICYT (Ministry of Education, Spain) for financial support.

---

[a]Permanent address: Departament d'Estructura i Constituents de la Matèria, Facultat de Física, Universitat de Barcelona, Diagonal 647, 08028 Barcelona, Spain.

[b]Present address: 515 Station Rd., Amherst, MA 01002.

[1] L. E. Tanner, A. R. Pelton, and R. Gronsky, J. Phys. (Paris), Colloq. **43**, C4-169 (1982); see also L. E. Tanner, Philos. Mag. **14**, 111 (1966).

[2] R. Oshima, M. Sugiyama, and F. E. Fujita, Metall. Trans. A **19**, 803 (1988); S. Muto, R. Oshima, and F. E. Fujita, Acta Metall. Mater. **38**, 684 (1990); S. Muto, S. Takeda, R. Oshima, and F. E. Fujita, J. Phys. Condens. Matter **1**, 9971 (1989).

[3] I. M. Robertson and C. M. Wayman, Philos. Mag. A **48**, 421 (1983); **48**, 443 (1983); **48**, 629 (1983).

[4] T. Onozuko, N. Ohnishi, and M. Hirabayashi, Metall. Trans. A **19**, 797 (1988).

[5] W. W. Schmahl, A. Putnis, E. Salje, P. Freeman, A. Graeme-Barber, R. Jones, K. K. Singh, J. Blunt, P. P. Edwards, J. Loram, and K. Mirza, Philos. Mag. Lett. **60**, 241 (1989).

[6] X. Jiang, P. Wochner, S. C. Moss, and P. Zschak (to be published).

[7] S. M. Shapiro, Y. Noda, Y. Fujii, and Y. Yamada, Phys. Rev. B **30**, 4314 (1984).

[8] S. M. Shapiro, B. X. Yang, G. Shirane, Y. Noda, and L. E. Tanner, Phys. Rev. Lett. **62**, 1298 (1986); S. M. Shapiro, J. Z. Larese, Y. Noda, S. C. Moss, and L. E. Tanner, Phys. Rev. Lett. **57**, 3199 (1986).

[9] H. Seto, Y. Noda, and Y. Yamada, J. Phys. Soc. Jpn. **59**, 965 (1990).

[10] L. E. Tanner, D. Schryvers, and S. M. Shapiro, Mater. Sci. Eng. A **127**, 205 (1990); D. Schryvers and L. E. Tanner, Ultramicroscopy **32**, 241 (1990); S. M. Shapiro, B. X. Yang, L. E. Tanner, and D. Schryvers, Phys. Rev. B **44**, 9301 (1991).

[11] L. P. Testardi, Rev. Mod. Phys. **47**, 637 (1975).

[12] L. Delaey, P. F. Gobin, G. Guenin, and H. Warlimont, in *Proceedings of the International Conference on Martensitic Transformations, ICOMAT-79* (MIT, Cambridge, 1979).

[13] C. Bequart, P. C. Clapp, and J. A. Rifkin, in *Kinetics of Phase Transformations,* edited by M. O. Thompson *et al.*, MRS Symposia Proceedings No. 205 (Materials Research Society, Pittsburgh, 1990).

[14] W. Petry, A. Heiming, and J. Trampenau (to be published); W. Petry, T. Flottman, A. Heiming, J. Trampenau, and M. Alba, Phys. Rev. Lett. **61**, 722 (1988); A. Heiming, W. Petry, J. Trampenau, M. Alba, C. Herzig, and G. Vogl, Phys. Rev. B **40**, 11426 (1989); A. Heiming, W. Petry, G. Vogl, J. Trampenau, H. R. Schober, J. Chevrier, and O. Scharpf, Z. Phys. B (to be published).

[15] These solutions have been noted for two dimensions by J. L. Ericksen [Int. J. Solids Struct. **22**, 951 (1986)] and A. E. Jacobs [Phys. Rev. B **31**, 5984 (1985)]. Our result also applies, *mutadis mutandis*, to three dimensions.

[16] A. Khachaturyan, *Theory of Structural Transformations in Solids* (Wiley-Interscience, New York, 1983), pp. 431–440. Khachaturyan also suggested [Proceedings of the Cornell Workshop on Martensitic Theory, 1989 (unpublished)] that tweed might be viewed as a spin-glass phase.

[17] G. R. Barsch and J. A. Krumhansl, Metall. Trans. A **19**, 761 (1988).

[18] K. Fuchizaki and Y. Yamada, Phys. Rev. B **40**, 4741 (1989); K. Fuchizaki, Y. Noda, and Y. Yamada, Phys. Rev. B **39**, 9260 (1989).

[19] R. G. Gooding and J. A. Krumhansl, Phys. Rev. B **38**, 1695 (1988); **39**, 1535 (1989); F. Falk, Z. Phys. B **51**, 177 (1983).

[20] P. C. Clapp, in Proceedings of the Workshop on Neutron Studies of Martensitic Transformations, Brookhaven National Laboratory, Upton, 14–16 March 1991 (to be published).

[21] S. Marais, V. Heine, C. Nex, and E. Salje, Phys. Rev. Lett. **66**, 2480 (1991).

[22] The 3D generalization of the constraint breakup (1) and of the Landau-Ginzburg free energy (2) are straightforward and numerical work should be possible, but the mapping onto a spin model may not be.

[23] R. Pirc, B. Tabic, and R. Blinc, Phys. Rev. B **36**, 8607 (1987).

[24] I. Ya. Korenblit and E. F. Shender, Zh. Eksp. Teor. Fiz. **89**, 1785 (1985) [Sov. Phys. JETP **62**, 1030 (1985)]; H. Takayama, Prog. Theor. Phys. **80**, 827 (1988).

[25] D. Sherrington and S. Kirkpatrick, Phys. Rev. Lett. **35**, 1792 (1975); G. Parisi, Phys. Lett. **73A**, 203 (1979); Phys. Rev. Lett. **43**, 1754 (1979), J. Phys. A **13**, L115 (1980); **13**, 1101 (1980); **13**, 1887 (1980); M. Mezard, G. Parisi, and M. A. Virasoro, *Spin Glass Theory and Beyond* (World Scientific, Singapore, 1987); K. Binder and A. P. Young, Rev. Mod. Phys. **58**, 801 (1986).

[26] F. E. Fujita, Mater. Sci. Eng. A **127**, 243 (1990).

[27] Materials parameters for FePd suggest that the local concentration coupling α_η must be much smaller than that indicated by $\partial T_M/\partial \eta_0$, and initial 2D simulation *without* elastic constraints does indeed show a large range of tweed even for a much smaller α_η (to be published).

[28] S. Muto, S. Takeda, R. Oshima, and F. E. Fujita, J. Phys. Condens. Matter **1**, 9971 (1989); Jpn. J. Appl. Phys. **27**, L1387 (1988).

[29] In three dimensions, a similar scaling analysis indicates that ξ is unstable, and the tweed modulation will occur at the level of the lattice constant $\xi \sim a$, and $L \sim a/\epsilon$.

[30] The left half of the phase diagram depicted here is the same as that for the replica-symmetry-breaking solution of the Sherrington-Kirkpatrick (SK) model [25]. Since each half of the replica-symmetric solution of the two-sublattice antiferromagnetic model is the same as the SK solution, we are assuming that the (correct) replica-symmetry-broken solution will be the same as Parisi's solution.