Martensitic Tweed and the Two-Way Shape-Memory Effect

James P. Sethna

Laboratory of Atomic and Solid State Physics, Cornell University
Ithaca, NY 14853-2501, USA
E-mail: sethna@lassp.cornell.edu

and

Christopher R. Myers
Cornell Theory Center, Cornell University, Ithaca, NY 14853, USA

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ABSTRACT

We briefly introduce tweed, which is found above the martensitic transition in a variety of shape-memory, high-T_c, and other materials. Based on our previous mapping of the problem onto a spin-glass model, we conjecture that the two-way shape-memory effect is due to tweed.

1. What are Martensites?

Martensites are crystalline materials which have undergone a crystalline shape transition. For example, many metals are body-centered cubic at high temperature, and change to face-centered cubic at low temperature: this can be done through stretching the crystal along one of the three cubic axes (figure 1).

We’ll be using a simple, two-dimensional model for the martensitic transition in this paper. Our model will be a square lattice at high temperatures, and a rectangular lattice at low temperatures (with two variants: tall-and-thin and short-and-fat).

You can imagine that, when the material is only partly transformed, there will be a lot of strain at the boundary! (Half is stretched, half not: how will it avoid tearing in between?) It manages by using the several different stretching directions! Figure 2 shows a photograph by Chunhwa Chu and Richard James (Dr. Chunhwa Chu, Ph.D Thesis, University of Minnesota, 1993) of the domain patterns in their experiment. The light region to the upper right might correspond to an undeformed, high temperature cubic region; the striped region on the lower left is composed of two variants, stretched in two different directions. By making thin layers of two variants, the material manages to have no net stretch at the boundary! The different variants are separated by what are called twin boundaries.

These twins are responsible for the shape-memory effect. If one takes a teapot made of the cubic, high temperature phase of a shape-memory martensite, and cools it through the martensitic transition, it won’t get tall and thin of course — it’ll stay macroscopically the same shape, but now will be made up of tiny slivers of

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aNot all changes in the crystal shape give martensites: for example, if the volume changes too much, the transition behaves quite differently and isn’t called martensitic.
various stretched variants, as in Figure 2. The teapot will be much easier to dent in the twinned state, since one no longer has to break bonds between atoms: one can change the shape by moving the twin boundaries and changing the relative amounts of differently stretched regions. If one pulls our model horizontally, one gets more of the tall-and-thin regions, and less short-and-fat (figure 3).

Now, crush the teapot into a ball. Heat the ball into the phase where it wants to be cubic (square). The ball uncrumples back into a teapot! Since no bonds were broken, and since the twin boundaries which moved during the crumpling vanish as the material is heated, it returns to its original shape. This is the (one-way) shape memory effect.
This paper is about the two-way shape memory effect. If one takes a shape-memory alloy, cools it, deforms it, and heats it, it returns to its original shape (one-way memory). If one cycles through cooling/deforming/heating many times, each time deforming in the same way, after tens or hundreds of cycles the material deforms by itself when cooled. This is quite a surprise! How can the boring, cubic phase (grey on the left in figure 3) remember how it should deform?

The community has proposals for what might store the memory. Real martensites do break some bonds as they transform, leaving dislocation lines: perhaps these remanents in the cubic phase induce the two-way shape memory. Also, these materials often have inclusions or precipitates: perhaps these deform during the cycling and induce future cycles to look like past ones. We’re proposing that these memories are stored in Tweed.

2. What is Tweed?

It turns out that, for tens to a hundred degrees above the martensitic transition temperature, that these shape-memory alloys aren’t boring, cubic materials as suggested by Figure 3. Instead, they exhibit cross-hatched patterns reminiscent of threads in a tweed jacket! Figure 4 shows a real picture of tweed: notice that the patchy regions occur in stripes along the two diagonals. Figure 5 shows our model of tweed, with realistic parameters (although the model, being two-dimensional, isn’t exactly completely realistic).

We’ve discussed our model in detail in the literature. (1) We blame the tweed on the inescapable, statistical fluctuations in the local concentration of the atoms in the alloy. The tweed domains are much smaller than the martensitic domains in figure 2 (nanometers rather than microns), and the dependence of the bulk transition temperature on the average concentration is strong (100K shift every 1% change in concentration). (2) Our numerical model is a Landau–Ginsburg theory, cooled by Monte Carlo: each little square represents one unit cell. (3) The tweed modulations are due to the elastic anisotropy: the bulk and diagonal shear elastic constants are much larger than the elastic constant for rectangular deformations (which mediate the transition). In the limit of infinite elastic anisotropy, we show that the only allowed deformations are the tweedy ones (superpositions of two one-dimensional modulations along the two diagonals). (4) The tweed becomes a thermodynamic phase in this infinite–anisotropy limit, and is precisely analogous to the frustrated spin-glass phase in random magnets.

This was an extremely satisfying explanation. We had claimed all along that working on spin glasses would one day help explain more practical materials. But skepticism in the field remains. Are the atomic deformations in tweed large enough for our anharmonic theory to be applicable? Are they due to the concentration fluctuations, or perhaps due to local geometries (large atoms and small atoms straining...
Fig. 4. Tweed as experimentally observed in transmission electron microscopy of a NiAl alloy (courtesy of Lee Tanner). Tweed is identified by its diagonal striations, which reflect some aperiodic lattice deformation with correlations on the scale of some tens of atomic spacings.
Fig. 5. Tweed as seen in our model. The darkness reflects the amount of diagonal strain (tall-and-skinny vs. short-and-fat). All materials parameters in our model are determined from independent experimental measurements in FePd alloys, except for the coupling to impurities. We set the coupling to impurities to fit the temperature range for the tweed deformation.
Fig. 6. The 2–Way Shape–Memory Effect. Cycling our model in an external field strains both the tweed and the martensite state. When the field is removed, the tweed springs back into its former, roughly cubic shape: the strain seems to have been forgotten. However, the strain largely reappears when the trained tweed is cooled into the low-temperature martensitic state. We propose that this is the cause of the two-way shape-memory effect.

the local lattice into different martensitic variants)? We wanted a clear, dramatic prediction from this exotic theory.

Glasses are not in equilibrium: their current state depends on the history of how they are prepared. Shape-memory alloys have a memory even in the high-temperature cubic state of strains applied at lower temperatures. What could be more natural than to store the memory in the glassy tweed state?

Sivan Kartha had gotten his doctorate and moved on to working for clean cars, so resurrecting the realistic simulation became a major endeavor. Instead, we set up a simple model in the infinite anisotropy limit (figure 6). Thus, the fact that the stripes run the full diagonal length of the system is forced by our model. We then tried training the tweed: cooling and heating in a field, then cooling and heating without. When the strain was removed, the tweed state returned to a roughly square state — but when cooled, the martensite was substantially stretched in the direction of the original strain. The tweed had been trained!

Plotting width versus time for a few runs (figure 7) leads us to believe that this wasn’t an accident. (1) The memory improved when we cooled and heated slowly.
Fig. 7. **Width versus time.** The graph shows four cycles in temperature from high (tweed) to low (martensite); the first two cycles are in an external field stretching horizontally (favoring the orange, short-and-fat, negative “width” state), the second two runs are without external field. Six out of eight runs agree: distort in the direction you’ve been trained in.

Of course, all deformations are incredibly slow on atomic time scales. (2) The transformation occurred in little bursts, or avalanches, something we’ve been studying in other contexts. (3) The training was much more rapid than in realistic materials: indeed, the second cycle often was an exact repetition of the first cycle. A larger and more realistic simulation would undoubtedly not repeat exactly after one cycle, but whether hundreds would be needed is an open question. Clearly, we should do a better job: we have (slowly) been gearing up to do simulations of much larger and more realistic systems.

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