

2014 von Kármán Prize

Materials from Mathematics

By Richard D. James

Like much of mathematics, the mathematical study of materials begins with Euler [7], or perhaps with Hooke's models of crystals as periodic arrays of balls ([8], Schem. 7). Some readers might know of a more recent historical touchstone, the $N - 6$ rule of von Neumann and Mullins [11, 16]. Scientists trained on both sides of the increasingly blurred line between mathematics and materials science have been attracted by the striking beauty of microstructure, the extreme nonlinearity, non-convexity, and even nonexistence exhibited by theories of materials, and the surprising links between the atomic structure of materials and a host of mathematical subjects, including geometry, calculus of variations, partial differential equations, group theory, graph theory, topology, and harmonic analysis. Mathematics is now guiding the discovery of materials using principles that in some cases run counter to accepted beliefs in materials science, and materials are inspiring new mathematics.

One of the most fruitful areas has been the study of phase transformations. There are a myriad of important phase transformations: solid to liquid, crystalline to amorphous, the ordering of atoms on a lattice, diffusional precipitation, and shape-changing transformations between crystalline forms without diffusion. The latter, called *martensitic phase transformations*, are particularly interesting because they can occur quickly. Highly ordered structures like crystals are famous for their "ferro" properties—ferromagnetism, ferroelectricity, ferroelasticity. The strongest materials and superconductors are also ordered materials. Having a phase transformation between two crystals with different ferro (or other) properties means that the material can be made to switch between these properties: in short, multiferroism by phase transformation. Some of the most interesting technological challenges today involve the possible application of these phase transformations to such fields as microelectronics, information storage, energy conversion, robotics, and sensing.

In nearly all of these applications, we want the material to pass back and forth through the phase transformation many times, through heating and cooling. (Ferroic martensitic materials, by the way, can often be made to transform at a fixed temperature, with the application of an electric or magnetic field.) Martensitic materials have a higher transformation temperature on heating than on cooling, a phenomenon known as hysteresis. The loop in a plot of phase-fraction vs. temperature is a *hys-*

terial to transform back and forth. Equally problematic for many applications is that the area enclosed by the hysteresis loop is a measure of the energy dissipated by the transformation.

What causes hysteresis? What governs the reversibility of phase transformations? In the pure element tin (Sn), the martensitic phase transformation that occurs around 10°C is so disruptive that during the first cooling cycle the material tears itself apart, yielding a pile of powdered tin. This is often attributed to a large volume change. Other textbook ideas for the origins of hysteresis include the "pinning" of interfaces by defects and the thermally activated crossing of energy barriers.

Mathematical theory suggests a quite different explanation. To understand this, we focus on the ubiquitous microstructure known as the austenite/martensite interface (Figure 1). During transformation, a lot of individual austenite/martensite interfaces make up the boundary between phases. We can understand its structure in part by solving

$$\inf_{\mathbf{y}} \int_{\Omega} W(\nabla \mathbf{y}(\mathbf{x}), \theta) dx, \quad (1)$$

where $\mathbf{y} : \Omega \rightarrow \mathbb{R}^3$ is a deformation that describes transformation and elastic distortion, θ is the temperature, and the infimum is taken over a suitable finite energy space. W has energy wells, whose precise form comes from careful x-ray diffraction measurements of the crystal structures of the two phases. The austenite/martensite interface is explained as a minimizing sequence of this energy, with $\theta = \theta_c$, the transition temperature. Several features, including the (finite) number of such interfaces, the angles seen in Figure 1, the full 3D structure, and the volume fraction of the bands on the left, are nicely predicted [1, 2].

What is not predicted by this argument is the fineness of the bands on the left. Here again, though, a better mathematical understanding is emerging [4, 5, 10]. The essential idea is that the boundary of each of these bands supports a small interfacial energy per unit area, which is not included in (1). Refining the bands drives the elastic energy in the transition layer between phases (calculated with (1)) to zero, but at the expense of increasing the total interfacial energy. Conversely, coarsening the bands reduces the interfacial energy but gives a big elastic energy. Figure 1 represents the compromise between these two energies. Their sum is a kind of coexistence energy. Whenever both austenite and martensite are present, the material has an additional positive coexistence energy.

But this suggests a reason for hysteresis based on metastability. Suppose that we start

temperature a bit more. If martensite appears, we also must accept a (positive) coexistence energy. This will disfavor the transformation to martensite. Mathematically, we should find an energy barrier [18].

The study of this barrier is in its infancy [19], but there is a very simple way to remove it. The energy wells of W have the form $\mathbf{R}\mathbf{U}$, where \mathbf{R} is a rotation matrix and \mathbf{U} is a positive-definite symmetric matrix. For the martensite, $\mathbf{U} \in \{\mathbf{U}_1, \dots, \mathbf{U}_n\}$ (determined completely from x-ray measurements*), whereas for austenite, $\mathbf{U} = \mathbf{I}$, the identity matrix. We could have an energy minimizer without either the elastic transition layer or the bands on the left of Figure 1, if there were a continuous function $\mathbf{y}(\mathbf{x})$ satisfying

$$\nabla \mathbf{y} = \begin{cases} \mathbf{R}\mathbf{U}_1, & \text{for } \mathbf{x} \cdot \mathbf{n} > 0, \\ \mathbf{I}, & \text{for } \mathbf{x} \cdot \mathbf{n} \leq 0 \end{cases} \quad (2)$$

for some 3×3 rotation matrix \mathbf{R} . As every undergraduate student in both mathematics and materials science should know [9], (2) holds if and only if $\lambda_2 = 1$, where λ_2 is the middle eigenvalue of \mathbf{U}_1 . The situation is pictured in Figure 2. When $\lambda_2 = 1$, the phases fit together perfectly. The reason for the complex microstructure in Figure 1 is precisely that $\lambda_2 \neq 1$!

How do we arrange to have $\lambda_2 = 1$? We are given the material, and either $\lambda_2 = 1$ or it does not. But every material has a composition. All its properties, including the value of λ_2 , can be modified by compositional changes. This has been done, guided by mathematical theory: New alloys were made, with the value of λ_2 systematically moved closer and closer to 1. The resulting alloy exhibits unprecedented low hysteresis [6, 17]. Earlier, people had made thousands of alloys, even in the systems where $\lambda_2 = 1$ has now been achieved to high accuracy. Why did people not, by accident, hit the composition for which $\lambda_2 = 1$? Hysteresis is so sensitive to λ_2 that, in most cases, they jumped over it. There is a singularity in the graph of the size of the hysteresis vs. λ_2 .

This is one way in which mathematics can discover materials: Identify special conditions on material properties at which interesting behavior, particularly singular behavior, is expected, then design compositional changes to achieve those conditions. This is an inverse problem. It can potentially be solved theoretically with first-principles methods, but many properties (including hysteresis) are not currently predictable by those methods. Much remains to be done, and multiscale mathematics is expected to play a central role.

Even stronger conditions of compatibility, called the *cofactor conditions* [3], have been achieved through systematic compositional changes. This recently led [14] to the fascinating alloy $\text{Zn}_{45}\text{Au}_{30}\text{Cu}_{25}$. It shows record low hysteresis for big first-order phase transformations (as low as 0.2°C) and remarkable reversibility. With its changing pattern of microstructure [12] during cyclic transformation, it is unlike any other martensitic material and begs for a dynamic analysis. Satisfaction of the cofactor, or even stronger, conditions in other material systems could lead to revolutionary materials, e.g., a shape-memory material that displaces NiTi, the most popular one (by far), or an oxide material that is able to go back and forth through a ferroelectric transformation many times without cracking.

Ferroic transformations suggest intriguing new applications. Imagine a martensitic alloy with one phase a strong magnet and the other nonmagnetic, and also with $\lambda_2 \approx 1$. If you transform the alloy by, say, heating, the magnetization will suddenly increase. Wrap a coil around the specimen, and, during transformation, a current will be induced in the coil. This is the direct conversion of heat to electricity (i.e., with-

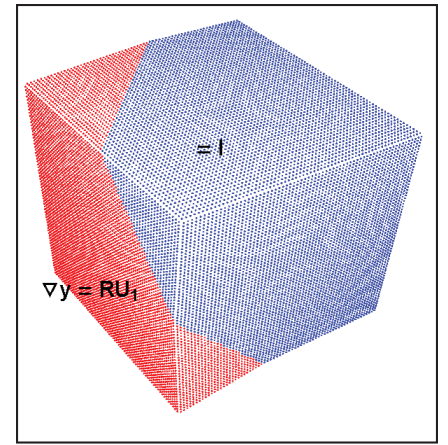


Figure 2. A perfect austenite/martensite interface is possible if and only if $\lambda_2 = 1$.

out a separate electrical generator [15]). Mathematically, it involves Maxwell's equations, micromagnetics, thermodynamics, and the theory of phase transformations [13]. Much remains to be understood about this method, and its many ferroic analogs, but it is a promising candidate for recovery of some of the vast heat energy created every day by diverse sources, from a data center to the sun.

Acknowledgments

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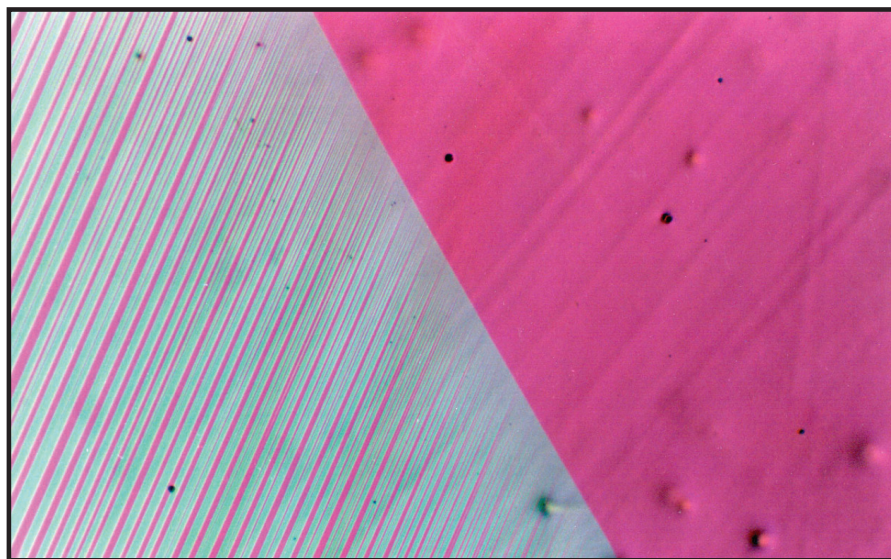


Figure 1. Austenite/martensite interface. The bands on the left are made up of two variants of martensite; the magenta region at the right is austenite. The total width of the original photograph is about 0.5 mm. Courtesy of C. Chu.

teresis loop. To achieve fast switching of phases, we want a small hysteresis loop, i.e., we do not want to have to heat and cool by hundreds of degrees just to get the mate-

rial in the high-temperature austenite phase and lower the temperature. We reach the temperature at which the two bulk phases have the same free energy, then we lower the

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