Phase Transformations in Smart Materials

Robert E. Newnham

*The Pennsylvania State University, Materials Research Laboratory, University Park, PA 16802, USA.
E-mail: bobnewnham@psu.edu*

Abstract

One of the qualities that distinguishes living systems from inanimate matter is the ability to adapt to changes in the environment. Smart materials have the ability to perform both sensing and actuating functions and are, therefore, capable of imitating this rudimentary aspect of life. Four of the most widely used smart materials are piezoelectric $Pb(Zr, Ti)O_3$, electrostrictive $Pb(Mg, Nb)O_3$, magnetostrictive $(Tb, Dy)Fe_2$ and the shape-memory alloy NiTi. All four are ferroic with active domain walls and two phase transformations, which help to tune the properties of these actuator materials. $Pb(Zr, Ti)O_3$ is a ferroelectric ceramic which is cubic at high temperature and becomes ferroelectric on cooling through the Curie temperature. At room temperature, it is poised on a rhombohedral–tetragonal phase boundary which enhances the piezoelectric coefficients. Terfenol, $(Tb, Dy)Fe_2$, is also cubic at high temperature and then becomes magnetic on cooling through its Curie temperature. At room temperature, it too is poised on a rhombohedral–tetragonal transition which enhances its magnetostriction coefficients. $Pb(Mg, Nb)O_3$ and nitinol (NiTi) are also cubic at high temperatures and on annealing transform to a partially ordered state. On further cooling, $Pb(Mg, Nb)O_3$ passes through a diffuse phase transformation at room temperature where it exhibits very large dielectric and electrostrictive coefficients. Just below room temperature, it transforms to a ferroelectric rhombohedral phase. The partially ordered shape-memory alloy NiTi undergoes an austenitic (cubic) to martensitic (monoclinic) phase change just above room temperature. It is easily deformed in the martensitic state but recovers its original shape when reheated to austenite. The structural similarities between these four superb actuator materials are remarkable, and provide a key to the development of future smart materials.

Robert E. Newnham recently retired as Alcoa Professor of Solid State Science at the Pennsylvania State University, where he taught courses in crystal chemistry, crystal physics and electroceramics. He has written more than 400 papers on ferroelectric and piezoelectric materials and devices, and is a member of the US National Academy of Engineering and the International Academy of Ceramics.

1. Introduction

The concept of a smart material can be illustrated with the smart shock absorber used to suppress road vibrations (Fig. 1). Inside the smart absorber developed by Toyota, there is a multilayer piezoelectric ceramic which has five layers for sensing road vibrations. The multilayer stacks positioned near each wheel of the auto also have about 100 layers which act as the actuator, all part of the same $Pb(Zr, Ti)O_3$ (PZT) ceramic. After analyzing the vibration signals, a voltage is fed back to the actuator stack and a response is made by pushing on the hydraulic system of the auto to enlarge the motion. In this way, the auto is able to analyze acceleration signals from road bumps and respond with a motion that cancels the vibration. This is the Toyota Electronic Modulated System, which produces force in the kilonewton range and displacements in the micrometer range.

In the smart shock absorber, the *direct piezoelectric effect* is used as a *sensor* by converting mechanical stress into an electrical voltage. Working through a feedback circuit, a larger electrical voltage with the appropriate frequency spectrum and phase angles is then applied to the piezoelectric material. Using the *converse piezoelectric effect*, the actuator creates a vibration that is out of phase with the incoming vibration and cancels it. In this device, the piezoelectric ceramic acts as *both* a sensor and an actuator.

This combination of sensing and actuating mimics two of the functions of a living system, namely being aware of the surroundings and then being able to respond to that signal with a useful response, usually in the form of a motion. By way of definition, then, a smart material is not simply a sensor. A sensor receives a stimulus and responds with a signal. A smart material is not simply an actuator. An actuator produces a useful motion or action. Smart materials function as both sensors and actuators. Smart materials sometimes have a control system and sometimes not. Some function like our spinal cord in that they are *passively smart* and respond without thought or signal processing going on. They are

analogous to the reflex responses of the human body. In other cases, smart systems analyze the sensed signal, perhaps for its frequency components, and then make a choice as to what type of response to make. An *actively smart system* such as this acts like a cognitive response in the human body (Newnham & Ruschau, 1991).

2. Molecular mechanisms

Crystallographic phase transformations are a prominent feature of the best smart materials. All four of the major families exhibit at least two transitions with different order parameters.

Nitinol and other shape-memory alloys have a broad phase transition with partially ordered caesium chloride-like structures transforming to a martensitic-like phase of lower symmetry. Both atomic ordering and atomic displacements are involved. In lead magnesium niobate (PMN), an outstanding electrostrictive material with the perovskite structure, there is a similar diffuse phase transition from a partially ordered high-temperature state to a ferroelectric low-temperature state. PMN is a ferroelectric analog to ferroelastic nitinol.

Terfenol is a typical magnetostrictive actuator with strong coupling between magnetic field and mechanical motion. It is an iron–rare-earth alloy with a paramagnetic-to-ferrimagnetic phase change at high temperature. Magnetostrictive actuators are operated near a second phase transformation where the magnetic spins undergo reorientation to different crystallographic directions. In piezoelectric PZT, the best known of the actuator materials, there are similar changes in symmetry. PZT is cubic at high temperatures and is operated near a boundary between rhombohedral and tetragonal states. Terfenol is a magnetic analog to ferroelectric PZT.

3. Ferroelectrics

To illustrate the behavior of piezoelectric and electrostrictive actuators, we have chosen $Pb(Zr, Ti)O_3$ and $Pb(Mg, Nb)O_3$, usually referred to as PZT and PMN, respectively. PZT (lead zirconate titanate) is a well behaved normal ferroelectric with a large spontaneous polarization appearing at the Curie temperature. PMN (lead magnesium niobate) is a relaxor ferroelectric with a partially ordered perovskite structure and a broad diffuse phase transition. Very large dielectric constants and electrostriction coefficients are observed in this temperature range.

The multimillion dollar market for PZT multilayer actuators includes d_{33} thickness mode transducers, d_{31} transverse mode transducers and various bender types. Multilayer actuators have about a hundred layers and overall dimensions in the millimeter to centimeter range. Piezoelectric printers, fuel injectors and pneumatic

valves are well developed markets for these multilayer actuators.

Multilayer actuators make use of ferroelectric oxides such as lead zirconate titanate (PZT) and lead magnesium niobate (PMN) with the perovskite structure. Ferroelectric oxides with the perovskite, tungsten bronze, pyrochlore and bismuth titanate layer structures all have high dielectric constants, high refractive indices, and large electromechanical coupling coefficients, and all contain corner-linked octahedral networks of Ti^{4+}, Nb^{5+} or other d^0 ions. These transition-metal elements are the highly polarizable 'active' ions promoting ferroelectricity and the high permittivities and piezoelectric constants required for transducers and capacitors. With reference to the periodic system, there are two major groups of active ions, and both are near electronic 'crossover' points where different types of atomic orbitals are comparable in energy and where hybrid bond formation is prevalent. The first group, typified by Ti^{4+}, Nb^{5+} and W^{6+}, are d^0 ions octahedrally coordinated to oxygen. For Ti^{4+}, the electronic crossover involves the $3d$, $4s$ and $4p$ orbitals, which combine with the s and p orbitals of its six O^{2-} neighbors to form a number of molecular orbitals for the $(TiO_6)^{8-}$ complex. The bond energy of the complex can be lowered by distorting the octahedron to a lower symmetry. This leads to molecular dipole moments, ferroelectricity, large dielectric constants, piezoelectricity and electrostriction. A second group of active elements contributing to polar distortions in ceramic dielectrics are the lone-pair ions having two electrons outside a closed shell in an asymmetric hybrid orbital. Among oxides, the most important of these lone-pair ions are Pb^{2+} and Bi^{3+}, which are involved in a number of ferroelectrics ($PbTiO_3$, $Bi_4Ti_3O_{12}$, $PbNb_2O_6$) with high Curie temperatures. In many of these compounds, Pb^{2+} and Bi^{3+} are in pyramidal coordination with oxygen and therefore contribute to the spontaneous polarization.
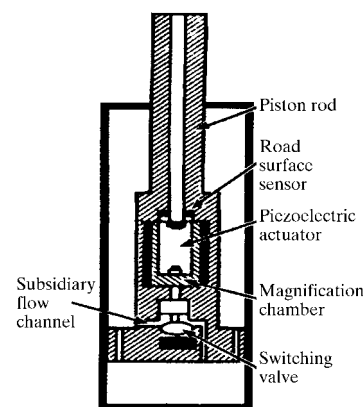

Fig. 1. Cross section of the principal portion of a shock absorber (Uchino, 1997).

3.1. *Piezoelectric PZT*

Most piezoelectric transducer formulations are based on $Pb(Zr, Ti)O_3$, one of a number of ferroelectric substances crystallizing with the perovskite structure (Megaw, 1957). Pb atoms are located at the corners of the unit cell and O atoms at the face centers. Both Pb and O ions have radii of about 1.4 Å and together they make up a face-centered cubic array having a lattice parameter near 4 Å. Octahedrally coordinated Ti or Zr ions are located at the center of the unit cell.

On cooling from high temperature, the crystal structure of PZT undergoes a displacive phase transformation with atomic displacements of about 0.1 Å. For titanium-rich compositions, the point symmetry changes from cubic $m3m$ to tetragonal $4mm$ at the Curie temperature. The tetragonal state with its spontaneous polarization along [001] persists down to 0 K. The structural changes are illustrated in Fig. 2.

To make use of these piezoelectric ceramics with their large polarizations, compositions near a second phase transition are chosen. At the Curie point, PZT converts from a paraelectric state with the ideal cubic perovskite structure to a ferroelectric phase located near a morphotropic phase boundary between the tetragonal and rhombohedral states. Very large piezoelectric coupling between electric and mechanical variables is obtained near this phase boundary. Much of the current research in this field involves looking for other morphotropic phase boundaries to further enhance the electromechanical coupling factors.

The two effects that are utilized in PZT transducers are the direct and the converse piezoelectric effects. The direct effect relates polarization to stress and is used in sensors. The converse effect relates strain to electric field and is used in actuators.

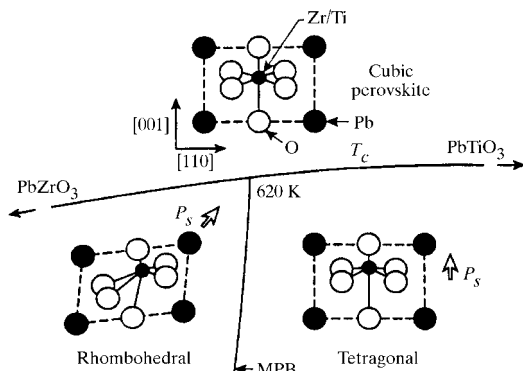For a poled ceramic having symmetry ∞m, d_{31}, d_{33} and d_{15} are the appropriate tensor coefficients. There are both intrinsic and extrinsic contributions to these piezoelecric coefficients. The intrinsic effects coming from the distortions of the crystal structure under mechanical stress are pictured in Fig. 3.

Under mechanical stress parallel to the dipole moment, there is an enhancement of P_s along X_3. When stress is applied perpendicular to that dipole moment, electric charges are developed transversely. These are the d_{33} and d_{31} effects, respectively. When the dipole is tilted by shear stress, charges appear on the side faces, the d_{15} coefficient. There are extrinsic contributions to the piezoelectric coefficient as well and these can be extremely large, often involving the domain wall motions.

Ferroelectric ceramics such as lead zirconate titanate do not become piezoelectric until electrically poled. Poling is carried out under intense electric fields at elevated temperatures below the ferroelectric Curie point where the domains are easily aligned.

Titanium-rich compositions in the PZT system favor a tetragonal modification with sizable elongation along [001] and a large spontaneous polarization in the same direction. There are six equivalent polar axes in the tetragonal phase corresponding to the [100], [$\bar{1}$00], [010], [0$\bar{1}$0], [001], [00$\bar{1}$] directions of the cubic paraelectric state. A rhombohedral ferroelectric state is favored for zirconium-rich compositions. Here the distortion and polarization are along [111] directions, giving rise to eight possible domain states: [111], [$\bar{1}$11], [1$\bar{1}$1], [11$\bar{1}$], [$\bar{1}\bar{1}$1], [$\bar{1}$1$\bar{1}$], [1$\bar{1}\bar{1}$] and [$\bar{1}\bar{1}\bar{1}$].

The compositions that pole best lie near the morphotropic boundary between the rhombohedral and tetragonal ferroelectric phases. For these compositions,

Fig. 2. A portion of the $PbZrO_3$–$PbTiO_3$ phase diagram showing the structure changes at the Curie temperature (T_c) and the morphotropic phase boundary (Jaffe *et al.*, 1971). Compositions near a morphotropic phase boundary have 14 possible poling directions.
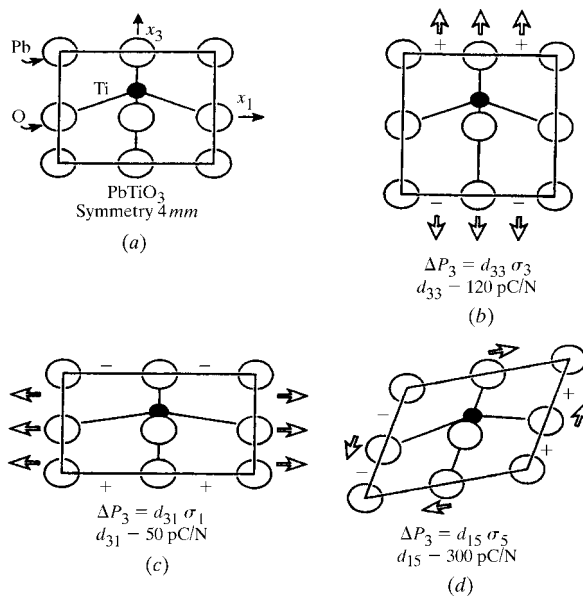

Fig. 3. Intrinsic piezoelectric effect in polar lead titanate.

there are 14 possible poling directions over a very wide temperature range. This explains in part why the ceramic piezoelectric coefficients are largest near the morphotropic boundary. Phase changes between the rhombohedral and tetragonal phases also occur during the poling process.

3.2. *Electrostrictors*

Piezoelectricity is a third-rank tensor relating strain and electric field. Electrostriction is a fourth-rank tensor relating strain to the square of the electric polarization.

Above the Curie temperature, the perovskite structure is cubic and the electrostriction effect is more important than the piezoelectric effect because third-rank tensors disappear in centrosymmetric media. This leads to what we call very smart ceramics. In a smart ceramic, the direct piezoelectric effect is used for sensing followed by feedback through the converse piezoelectric effect. In a very smart material, we monitor the change in capacitance of the material. We then monitor feedback with both direct-current (DC) and alternating-current (AC) fields to tune the magnitude of the electromechanical-coupling coefficient and then to drive it. For higher-order coupling coefficients like electrostriction, there are three rather than two coupled effects: the change in the dielectric constant with stress, the field dependence of the piezoelectric voltage coefficient and the electrically driven mechanical strain. The electrostrictive ceramic becomes a tunable transducer (Newnham, 1991).

We began work on a number of these electrostrictive materials nearly 20 years ago (Uchino *et al.*, 1980) for active optic systems. Much of this work was performed with the ITEK Corporation in Lexington, MA, USA. During the cold war, there were many satellites flying over the old Soviet Union utilizing active optic systems to eliminate atmospheric turbulence. In adjusting the position of optical components, electrostrictive materials have an advantage over piezoelectrics because there is much less hysteresis associated with the motions.

Work on active optic systems has continued over the years and similar multilayer actuators were used to correct the positioning of the optical elements in the Hubble telescope. Supermarket scanners use actuators and flexible mirrors to optically interrogate bar codes.

3.3. *Relaxor ferroelectrics*

Ordered perovskites generally have low dielectric constants because the linkage between 'active' ions is severed. In partially disordered structures such as the relaxor ferroelectrics, the dielectric constant can be extremely large, making them useful as capacitor dielectrics and as electrostrictive actuators. The most widely used compositions are modifications of lead magnesium niobate, $Pb_3MgNb_2O_9$.

Relaxor ferroelectrics consist of temperature-sensitive microdomains resulting from the many different 'active' ion linkages in the disordered octahedral framework. Each NbO_6 octahedron may be bonded to anywhere from zero to six other NbO_6 octahedra. Connections between these octahedra are assumed to be essential to ferroelectricity and high dielectric constant values. As temperature decreases from the high-temperature paraelectric state, ferroelectric microdomains gradually coalesce to macrodomains giving rise to a diffuse phase transformation. These polarization fluctuations are also dependent on bias field and measurement frequency. The dielectric constant drops off rapidly with frequency (hence the name 'relaxor') because it takes time for the polarization fluctuations to respond. DC bias fields favor coalescence, giving the same effect as lowering the temperature.

Relaxor behavior is very common along Pb-based perovskites, suggesting that Pb^{2+} and its 'lone-pair' electrons play a role in the microdomain process, possibly by adjusting the orientation of the lone pair.

Electrostriction is described by a 6×6 matrix, Q, relating strain to the square of the electric polarization. This type of matrix is familiar to most materials scientists because electrostriction is a fourth-rank tensor almost identical in form to elasticity. For a cubic crystal, we are dealing with the same coefficients, 11, 12 and 44, that would normally be used to describe the elastic properties of a cubic crystal. In the case of electrostriction, strain is induced electrically rather than mechanically.

Compared to piezoelectric transducers which utilize a polar material, electrostrictive transducers use a cubic material, a material that is poised on an instability with micro regions that are fluctuating in polarization. On average, the atoms are located in the ideal cubic sites but are continually shifting off these positions. An atomic view of the Q_{11}, the Q_{12} and the Q_{44} motions (Newnham, 1991) in an electrostrictive material is shown in Fig. 4. The underlying origin of these effects is a partial ordering of the PMN perovskite structure in which the Nb and the Mg atoms of lead magnesium niobate alternate but only over short ranges, typically 30–50 Å, just a few unit cells. Within these ordered islands, there are fluctuating dipoles that are acted upon by an external field to make large electrostrictive motion.

4. Magnetostrictive actuators

PZT and PMN ceramics are outstanding ferroelectric actuators, but equally interesting developments are taking place in ferroelastic and ferromagnetic materials. All these ferroic materials have a domain structure in which the walls can be moved with electric fields, magnetic fields or mechanical stresses.

Magnetostrictive alloys like terfenol-D ($Tb_{1-x}Dy_xFe_2$) function well as both sensors and

actuators (Hathaway & Clark, 1993). High-power actuators can deliver forces greater than 50 MPa with strains up to 0.6%, while magnetostrictive sensor materials can provide hundreds of times the sensitivity of semiconductor strain gauges. Magnetoelastic materials also have tunable elastic moduli that can be controlled by external magnetic fields.

A large number of magnetomechanical transducers and actuators utilizing terfenol-D have been designed and manufactured. The high-energy density of these actuators, plus their ruggedness and reliability, make them attractive for vibration suppression and high-power sonar. Thin films of magnetostrictive rare-earth–iron alloys can be sputtered on silicon and patterned by etching or sputtering through masks. Micropump and microvalve membranes and cantilevers appear to be promising microelectromechanical systems (MEMS) components (Wun-Fogle et al., 1987).

The rare-earth atoms in terfenol have large orbital moments that interact with magnetic fields to give large magnetostrictive strains. Rotation of the magnetization is largely responsible for the shape change. The field-induced strain in terfenol-D is about a hundred times larger than those in iron and nickel.

The iron in terfenol produces the high Curie temperature. The rare-earth Tb and Dy atoms produce the large magnetostriction. In combination, these three elements produce useful alloys. What I wish to point out here is the analogy to PZT. Plotted in Fig. 5 is a portion of the magnetic phase diagram of the material. It is cubic and paramagnetic at high temperature and then undergoes a magnetic phase transformation to a rhombohedral structure with magnetic spins parallel to $\langle 111 \rangle$ directions. Near room temperature, it is poised on an instability with the spins ready to reorient into the tetragonal directions, the former $\langle 100 \rangle$ directions of the cube. There is a complex domain structure both above and below the transition and, like PZT, it is poised on a rhombohedral–tetragonal phase boundary. The phase diagram of terfenol is the magnetic equivalent to the morphotropic boundary of PZT.

The figure of merit for magnetostrictive actuators is proportional to the saturation strain coefficient. But, in addition to a large shape change, the strain must be easy to move. Therefore, the anisotropic coefficient K, which controls the rotation of the magnetization, also comes into the figure of merit, λ/K, where λ is the saturation strain. $TbFe_2$ has a very large λ coefficient, but also has a large anisotropy constant K, which reduces the figure of merit. $DyFe_2$ has an anisotropy coefficient of opposite sign. So by tuning the composition to be near the point where the anisotropy coefficient goes to zero, one can make an easily movable strain in this magnetostrictive alloy. This maximizes the figure of merit.

Fig. 6 shows the two magnetic phase changes for terfenol-D. At high temperature, it is paramagnetic and,
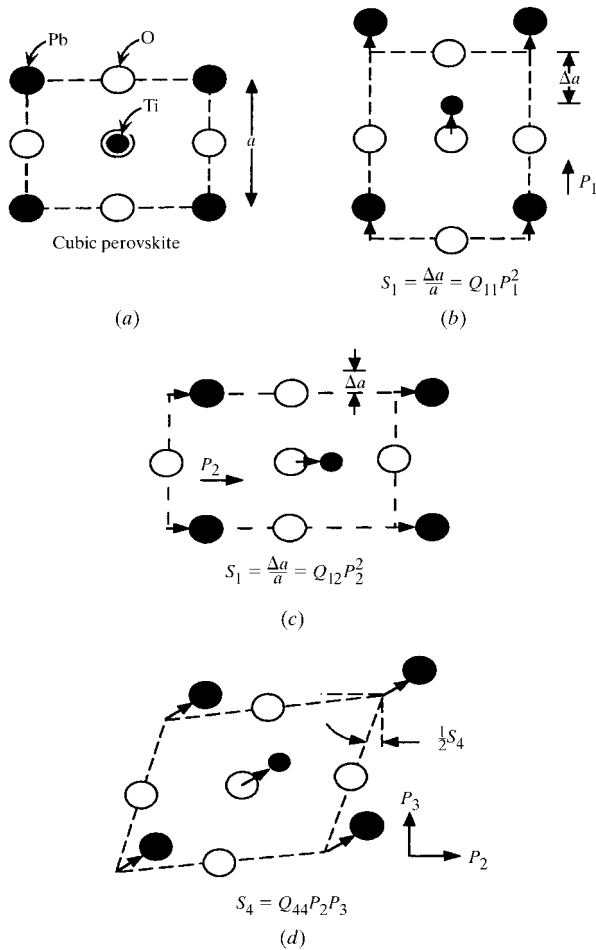
Fig. 4. Electrostriction in cubic perovskites showing the physical origin of the electrostrictive coefficients Q_{11}, Q_{12} and Q_{44}.
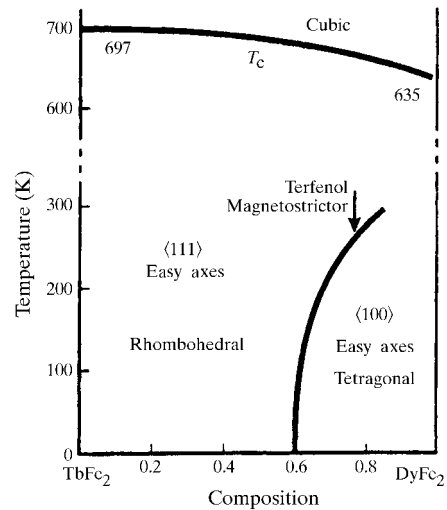
Fig. 5. Binary phase diagram for the $Tb_{1-x}Dy_xFe_2$ system. Compositions near the magnetic spin boundary at $x = 0.7$ are used in magnetostrictive applications (Purdy & Parr, 1961).

below T_c near 700 K, the spins are aligned along a [111] direction giving a rhombohedral distortion of the unit cell. The strong antiferromagnetic interactions between the iron and rare-earth spins make the alloy ferrimagnetic rather than ferromagnetic. Near room temperature, there is a spin reorientation to the tetragonal ⟨100⟩ directions of the cube. The magnetic point group changes from $3m'$ (the prime indicating time reversal operator) to $4/mm'm'$.

An explanation of the large magnetostrictive effect in $TbFe_2$ and rare-earth–iron intermetallic compounds has been put forward by Clark and co-workers (Clark, 1980). Pure rare-earth metals possess large magnetostrictive strains but are not used as actuators because of their low Curie temperatures. When alloyed with iron, however, the RFe_2 compounds are magnetic at room temperature with T_c values near 700 K.

The large magnetostriction coefficients are caused by the orbital motion of the rare-earth $4f$ electrons, which impart a shape anisotropy to the atoms. Trivalent Tb and Dy ions resemble flattened oblate ellipsoids while Er, Sm and Tm ions have elongated prolate shapes. Under strong magnetic fields, the magnetization rotates to a new orientation and is accompanied by a shape change as the ellipsoids change orientation.

The resulting magnetostrictive strain is especially large for RFe_2 compounds with the cubic Laves $C15$ structure. The structure distorts to a pseudocubic ferrimagnetic phase below the Curie temperature with the iron sublattice magnetization opposed to that of the rare earths. At room temperature, the preferred directions for magnetization are the six ⟨100⟩ cube axes for domains in $DyFe_2$. For $TbFe_2$, the eight ⟨111⟩ body diagonals are the easy axes of magnetization.

The magnetostriction coefficients are largest for the rhombohedrally distorted alloys with ⟨111⟩ easy axes. This can be understood by examining the crystal structure. In the $C15$ structure, the rare-earth ions form a diamond-like lattice in which each rare-earth atom is bonded along ⟨111⟩ directions to four other rare-earth

atoms. When a magnetic field is applied along [111], and the RFe_2 compound magnetizes in this direction, there is a redistribution of electron density and a change in the $R-R$ bonding. For oblate atoms like terbium, the bonds along ⟨111⟩ are enhanced when the $4f$ electron contribution to the Tb—Tb bond along [111] is decreased. This causes expansion along [111] and contraction in the perpendicular directions. For $ErFe_2$, the prolate Er ions also align along ⟨111⟩ directions but a field along [111] causes a contraction along [111] rather than an expansion. In this case, the Er—Er bond along [111] grows stronger and shorter as magnetization develops along [111]. Thus, $TbFe_2$ has a large positive magnetostriction coefficient and $ErFe_2$ has a large negative coefficient.

Other RFe_2 compounds magnetize along ⟨100⟩ directions and have rather modest magnetostrictive coefficients. The enhancement in electron density is the same for all four $R-R$ bonds pointing along different ⟨111⟩ directions. This applies to both oblate and prolate rare-earth atoms. As a result, the magnetostriction coefficient of $DyFe_2$ is an order of magnitude smaller than that of $TbFe_2$.

Nevertheless, it is important to alloy $TbFe_2$ with $DyFe_2$. In actuators and transducers, it is very useful to have a large shape change but it is also important to be able to control the shape change with small applied fields. A large shape change frozen in position is of no practical value. To lower the driving field, a second phase change is positioned near room temperature. This can be performed by lowering the Curie temperature but this has the effect of demagnetizing the actuator and greatly reducing the magnetostriction coefficient. It is preferable to choose a composition near the rhombohedral–tetragonal phase boundary where the easy axis switches from ⟨111⟩ to ⟨100⟩. Compositions near $Dy_{0.7}Tb_{0.3}Fe_2$ have large magnetostrictive coefficients with easily controlled shape changes. Below room temperature, the magnetic symmetry changes from rhombohedral to tetragonal with a large decrease in the magnetostrictive shape change.

Fig. 6. Magnetic phase transformation in terfenol-D, $Tb_{0.3}Dy_{0.7}Fe_2$, magnetostrictive actuator. At the Curie temperature, the paramagnetic phase converts to a rhombohedral ferrimagnetic phase (b) with spins parallel to ⟨111⟩ directions. Under operating conditions near room temperature, terfenol is poised on a second transition to a tetragonal ferrimagnetic state (c) with spins parallel to ⟨100⟩ axes.

5. Shape-memory metals

My last example of an actuator material involves the shape-memory alloys that are thermally driven rather than the magnetic drive of magnetostrictors or the electrical drive of piezoelectric and electrostrictive materials. This material too has phase transitions associated with the large thermomechanical coupling coefficients. A commonly used material is nitinol, nickel titanium alloys, investigated initially at the Navy laboratories. Working near 1:1 compositions, the nickel–titanium intermetallic compound melts congruently at about 1570 K and has a martensitic phase transformation near room temperature.

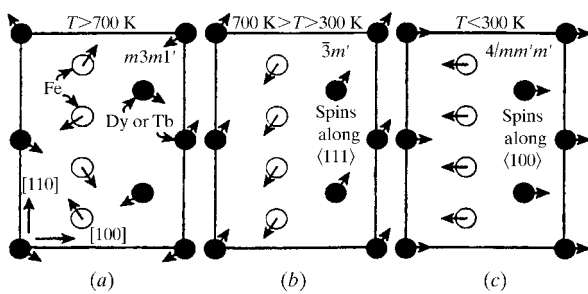Shape-memory alloys undergo martensitic transformations similar to those observed in the processing of

steel. Two characteristics of martensitic phase changes are the absence of long-range diffusion and the appearance of a shape change (Wayman, 1993). Ferroelastic phase transformations are also distortive and diffusionless, and have much in common with the martensites. Ferroelastic crystals exhibit mechanical hysteresis between stress and strain caused by the stress-induced movement of domain walls. Martensites are also internally twinned but mechanical stress causes phase changes as well as domain-wall movements.

Typically, these materials are partially ordered as they undergo a transition from a body-centered cubic structure to a partially ordered CsCl structure (Fig. 7). The shape-memory effect takes place at a martensitic transformation from the caesium chloride-like structure into a distorted multidomain martensite phase. Under stress, the martensite easily deforms and when re-heated goes back to the original morphology of the high-temperature structure. This is the shape-memory effect.

Some of the martensitic structures are very complex (Fig. 8). The monoclinic structure of nickel–titanium belongs to point group $2/m$ and has a β angle about $8°$ different from $90°$. This generates a large spontaneous strain accompanying the martensitic phase change and is the shape change that external mechanical stresses and thermally induced stresses act upon. In the case of

ferroelectrics, external fields act upon electric dipoles. For magnetic actuators, there are magnetic dipoles and with ferroelastics there is a shape change.

In the diffuse martensitic phase change, the partially ordered high-temperature austenite phase partially transforms into the martensitic phase (Fig. 9). Then, under mechanical stress, two things happen. Domain reorientation takes place as indicated by the little bars in Fig. 9 and phase changes occur as well. This behavior is very similar to the electrical behavior of the PMN relaxor ferroelectrics.

High-performance products utilizing shape-memory alloys include aircraft hydraulic couplings and electric connectors where they are used as substitutes for solenoids, motors and bimetallic actuators. Additionally, the alloys are used in shower heads and cut-off valves to provide thermal protection, and in dental prostheses and other medical products.

6. Concluding remarks

There are several common themes in this discussion of piezoelectric, electrostrictive, magnetostrictive and shape-memory materials. Two transformations are involved in most of these smart materials, often a primary ferroic (ferroelastic, ferroelectric or ferromagnetic) with domain-wall motions that assist in the sensing and actuating processes. The ferroics are operated near an instability to make these domain walls with their associated dipoles and strains movable. We have identified two main types among the commonly used actuators, although others appear to be possible too. In one type, there is a high Curie temperature as in PZT or terfenol and the actuator is operated near an orientational change of the electric or the magnetic dipole moment.

The second type involves a partially ordered phase, as in electrostrictive PMN or the shape-memory alloys. These materials are operated near a diffuse phase transition with two coexisting phases, the high
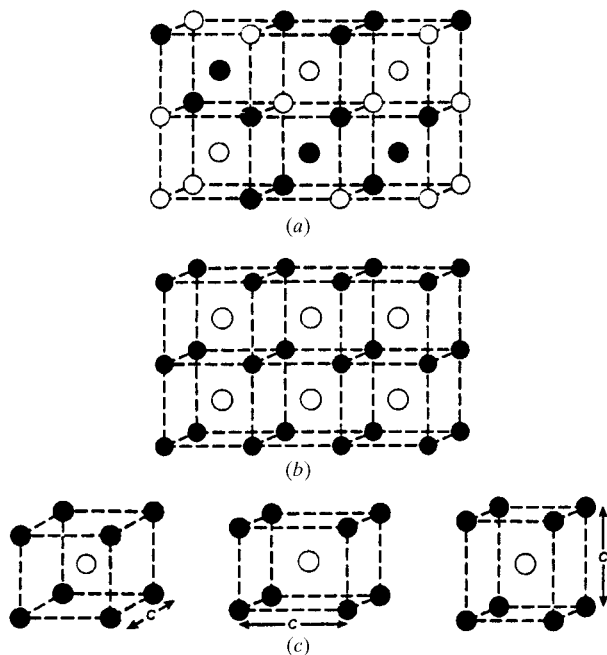
Fig. 7. Body-centered intermetallics often show a structural transformation from a high-temperature disordered body-centered-cubic phase (space group $Im3m$) (a) to an annealed-ordered austenite phase with the CsCl structure (space group $Pm3m$). (b) At lower temperatures, there is a second phase transition from austenite to a twinned martensite phase, pictured here as three variants of a body-centered tetragonal phase (space group $P4/mmm$) (c) with ferroelastic and antiphase domain walls.
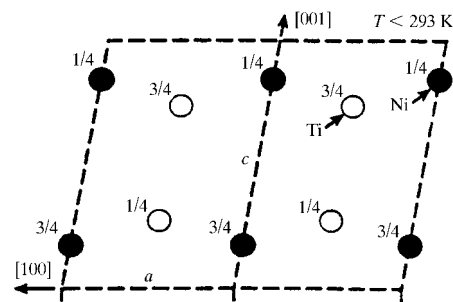
Fig. 8. Crystal structure of the martensite phase of nitinol, NiTi. The space group is $P2_1/m$ with lattice parameters $a = 2.884$, $b = 4.110$, $c = 4.665$ Å, $\beta = 98.10°$. Sometimes referred to as the low AuCd structure, there are 12 orientation states of this monoclinic phase with respect to the cubic austenite phase (Kudoh et al., 1985).

temperature or austenite-like phase and the low-temperature or martensitic type phase.

The underlying reasons are fairly obvious. Why use a primary ferroic? These provide a big handle for external fields or forces, whether it be a strain or an electric dipole or magnetic dipole. Why use a cubic prototype phase? The answer is that it gives many equivalent orientation states and makes is possible then to use polycrystalline materials without the necessity of growing single crystals. Why is partial ordering helpful? This type of structure provides many nucleation sites for generating a diffuse phase transformation. Why is a morphotropic transition used? This kind of instability ensures persistent disequilibrium over quite a wide range of temperatures.

In his recent book, *Out of Control*, author Kevin Kelly (1994) describes how biological systems evolve into more complex life forms: neither constancy nor relentless change will support a complex dynamic system. Equilibrium is death and complete chaos leads to explosive behavior, also followed by death. On the other hand, persistent disequilibrium optimizes dynamic behavior by staying on the hairy edge of rapid response (Kelly, 1994). The behavior of the sensor and actuator materials used in smart systems appears to be consistent with this idea.

As we look to the future, many new types of smart systems will be developed. Aerospace engineers are interested in smart air foils to control drag and turbulence. Diabetics need medical systems to sense the sugar level and deliver insulin. Architects are designing smart buildings that incorporate selfadjusting windows to control the flow of energy into the house. Tennis players will want smart racquets to make overhead smashes and delicate drop shots. Smart systems will identify burglars and other dishonest people and control their movements. Smart toilets are capable of analyzing urine to identify health problems. Smart irrigation systems are needed to optimize the world's food supply. Fish are the leading source of protein in many parts of the world. We can farm the oceans using smart transducers to talk to the fish and herd them like cattle. The word 'smart' is being used everywhere including the comic strips. Dagwood and Blondie recently visited a used car dealer who told them about a smart car, and they asked what is meant by a 'smart car'? The dealer replied that the car is so smart that if the payments are not made, it will drive itself back to the dealership!
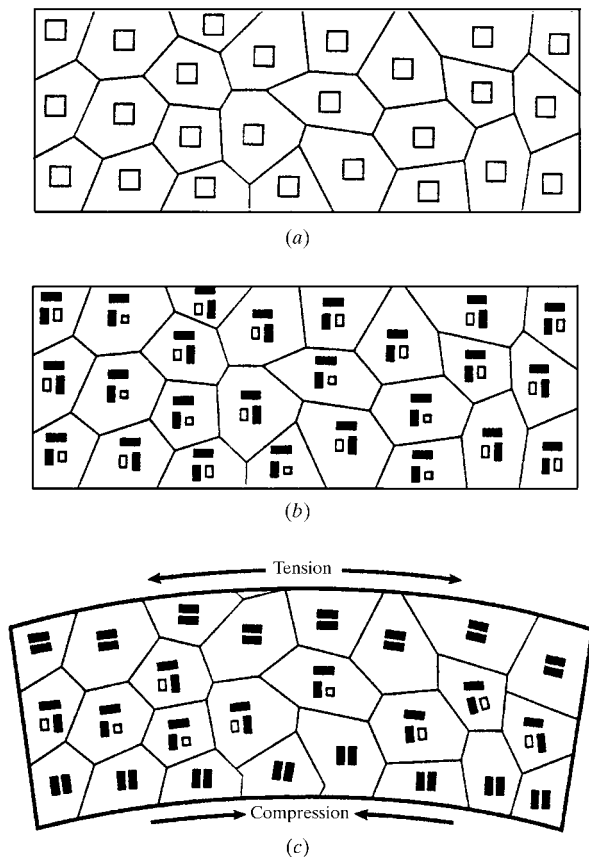
Fig. 9. Shape-memory alloys transform from a partially ordered high-temperature cubic austenitic phase (*a*) to a mixed austenite–martensitic partially transformed low-temperature state (*b*) at the operating temperature. When deformed under mechanical stress (tension and compression) (*c*), phase changes and domain-wall movements take place. The metal returns to its original shape when the austenite phase reappears under heating (deLange & Zijderveld, 1968). Both twin orientation and phase changes occur.

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