Title:

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Materials: Beyond Global Crystallographic
Analysis**

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Submitted to:

DOE Office of Scientific and Technical Information (OSTI)

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**Intrinsic Fine-Scale Structure in Complex Materials:
Beyond Global Crystallographic Analysis
(LDRD project # 97016)**

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Abstract

Many important classes of materials owe their interesting properties to structures and patterns produced by local atomic deviations from ideal crystallographic positions. The pattern scale may vary from a few atomic spacings to many microns. In a macroscopic sample these deviations may still average to an ideal lattice while retaining the intrinsic fine-scale structures, or a phase transition may create a pattern of variants of a new crystallographic structure. We have carried out experiments on the formation of fine-scale structures in a range of materials, particularly those produced by phase transitions. We have used Resonant Ultrasound Spectroscopy for elastic properties and dissipation, neutron pair-distribution function, and electronic transport measurements to characterize samples. We have carried out extensive dynamical modeling based on Ginzberg-Landau formalisms to simulate the development and appearance of the structures. Our results highlight the importance of long-range strain fields and the intrinsic unstable equilibrium features of the materials studied.

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Background and Research Objectives

The thermodynamically preferred state of all solids should be one in which all the atoms lie in an ordered array – a single crystal. Unless some care is taken, however, most materials solidify into an aggregate of small regions of single crystal material. In a metal, these regions are called grains. They are randomly oriented crystallites and are generally of order microns in size. It is well known that in steel the grain size determines many of the mechanical properties and the history of steel is greatly concerned with the processes which control grain size. Most materials exhibit this kind of division into small regions – generally called microstructures since their size can vary from a few atomic spacings to many microns. Within a region, which may be called a grain, crystallite, stripe, or domain, there is some uniform property – an orientation of crystal axes, a particular phase or structure, or an orientation of a magnetic or electric dipole moment.

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The properties of neighboring regions may have randomly differing values or they may bear some strict relationship – for example, the directions of the crystal axes may have to be at 90° to their neighbor's. Boundaries exist between regions, and depending on the property of interest, may be called grain or twin boundaries, or domain walls.

Microstructures are commonly formed at solid-solid phase transformations, where changing conditions like temperature, pressure or magnetic field on a solid forces a reorganization of the atoms. A carefully grown single crystal of a “parent” phase may thus be turned into a microstructured polycrystal of the new phase. The new phase starts to grow (“nucleates”) at many places, usually “weak spots” or defects, simultaneously in the parent material. Variants of the new phase (e.g. crystal axis directions) growing from each nucleation site eventually meet and form boundaries, creating the microstructure. In some materials, the atoms reorganize in a way that bears a strict relationship to the parent phase, and thus the regions of the new phase have some relationship. The movement is subtle, much less than an atomic spacing, then the possibility exists of being able to recover *exactly* the parent phase crystal on reversing the phase transformation conditions. In order to understand the effects of microstructures on macroscopic scales and the forces at work to determine the scale and form of the microstructures, we have directed a combined experimental and theoretical effort into materials from two classes which fall into this category, oxide perovskites and martensites. Both these classes are scientifically fascinating and are already used in various technologies, but there is still a poor understanding of the fundamental processes that create microstructures in them. High-Tc superconductors, Colossal Magnetoresistance (CMR) materials and a large number of ferroelectric materials fall into the oxide perovskites, which have the common structural feature of a metal atom surrounded by a rhombohedron of six oxygen atoms. Distortions of these rhombohedra – tilts, rotations, elongations – determine the microstructures and along with them, dramatic changes in electronic properties. Steels and shape-memory alloys fall into the martensites, although only the shape-memory alloys exhibit the reversibility mentioned above. Complex new crystal structures are formed in the microstructure by shearing forces in the parent phase, accompanied by large changes in the mechanical properties.

The *strain* in a lattice is a measure of how much atoms have moved relative to each other, away from a relaxed equilibrium situation. Strain can be measured by x-ray, neutron and electron diffraction at the atomic level, and by various mechanical methods at the macroscopic. The macroscopic effects of strain are most sensitively measured in the elastic constants, which relate stress and strain, and are second derivatives of the free energy, an important thermodynamic quantity.

Strain is also the theoretical parameter that controls these structural transformations in the Ginzberg-Landau (G-L) free energy expansion approach.

We have combined expertise from three main areas at LANL: elastic property measurement by Resonant Ultrasound Spectroscopy (RUS), a powerful and versatile technique developed at LANL and in which LANL is a recognized world leader; neutron pair-distribution function (PDF) analysis, an atomic-scale probe technique in which LANL had recognized expertise; and computer modeling of phase transformations in martensites using a G-L formalism, where we have both expertise and computer power. We intend to study and model a group of materials to understand the fundamentals of formation of microstructures and the ultimate effect on macroscopic properties, with the hope of identifying common features across these classes and providing the basis for control of various functionalities in new materials.

Importance to LANL's Science and Technology Base and National R&D Needs

Phase transformations that result in microstructures form the base of many technological materials. Hardened steel is perhaps the most common example. Many of the actinide materials used in the lab's defense missions undergo martensitic transformations, which are poorly understood. This research contributes to that understanding. Control of the mechanical, magnetic and electrical properties of materials produced by microstructuring has traditionally been approached empirically, due to the fact that a unified theoretical picture is not available to "design" materials with specific functionalities. An understanding of microstructures in solid-solid phase transformations is the goal of many researchers worldwide and results in this field have consequences for understanding a vast range of materials properties applicable to stockpile stewardship, and also for approaching the technological goal of "designer" materials.

Scientific Approach and Accomplishments

The materials we have studied are the oxide perovskites SrTiO_3 and the CMR material $\text{La}_{0.83}\text{Sr}_{0.17}\text{MnO}_3$, for the martensites, we have restricted ourselves to the B2 phase cubic alloys AuZn , NiTi , and $\text{Ni}_{0.62}\text{Al}_{0.38}$ because this is a simple parent phase and identical structures help in making comparisons.

We have single crystals of the perovskites and single crystals, polycrystals and powders of the high temperature phase of the martensites. Creating the oriented single crystal samples for RUS occupies much of the time in these experiments.

RUS measurements of the spectrum of resonant frequencies of the samples can provide (after fitting to a model of a homogenous elastic solid) the complete elastic matrix and the internal friction or dissipation of each mode, as a function of temperature between 4K and 900K. The dissipation is particularly useful because the most common mechanisms for dissipating acoustic energy are motion of boundaries and defects, and so is an indicator of microstructures. RUS samples are mounted so they contact the measuring sensors only at the corners, [1] and no surface contacts are needed. This is particularly useful for the martensites, where the formation of the microstructured martensite creates surface relief which renders surface mounted transducers inoperative. Much information can be obtained from the temperature behavior of the resonance frequencies without actually determining the elastic constants from the fitting procedure.

Neutron PDF measurements use the powdered samples. Measurements are made at the GLAD spectrometer at Argonne National Laboratory over the temperature range 20-300K. Counting-statistics and time-limitations mean that data points were taken only every 20K. We have extensive data on the $\text{Ni}_{0.62}\text{Al}_{0.38}$ sample and some on the AuZn sample, but a strong neutron absorption resonance in Au decreases the statistics in the AuZn case. The data is essentially fourier transformed to provide a spectrum of the separation of pairs of scattering centers. This provides information on strains in the lattice at an atomic scale.

Martensites

These materials transform from a high temperature phase (austenite) into a microstructured low temperature phase (martensite). Figure 1 is a bright-field HREM photograph of two variants of martensite in $\text{Ni}_{0.62}\text{Al}_{0.38}$. This appears within a single crystal of austenite. The shear, which drives the transformation, produces twins with parallel boundaries. Figure 2 shows RUS data on $\text{Ni}_{0.62}\text{Al}_{0.38}$, in three different forms. (a) is material quenched in the arc-melter, it has very small crystallites and lots of internal stresses. There is no apparent transformation, and the temperature coefficient dF/dT is negative as expected for a normal elastic solid. (b) is the same material after annealing, which relaxes much of the quench stress and increases the size of the grains. dF/dT is now positive for the austenite, and a well-defined phase transformation is apparent near 75K. There is hysteresis of about 10K apparent verifying the first-order nature of the transformation. (c) shows single-crystal data. An effect shows up before the main transformation temperature which also shows a first order nature.

This bump has been observed before [2] but the authors thought it was a surface effect. RUS is not surface sensitive: this is a real volume phase transformation preceding the main transformation which is not seen in the polycrystal. (d) is a close-up of the first line. It is a mode dependent on the weak shear modulus that drives the transformation, and with it, the peak width, which is proportional to the damping coefficient or dissipation of the material. The dissipation shows peaks at the two-phase transformations, as expected, but two new features are observed; a third broad peak below the transformation, and a remarkable upturn in the elastic modulus at very low temperatures. We expect the martensite to display high damping due to the possible motion of twin boundaries, but at very low temperatures this is a poor explanation, and the upturn is unexpected, since thermodynamics requires a flat slope as T approaches 0°K . This behavior is not what we expect of a twinned microstructure, but as figure 4(b) shows it is not unusual for a glassy material. This may be the first observation of glassy behavior in martensite, since RUS can make measurements where other techniques have difficulty. AuZn and NiTi both share this feature. Figure 3 shows PDF results for $\text{Ni}_{0.62}\text{Al}_{0.38}$. Each peak corresponds to a pair distance (labeled for the austenite in (b)). In (a) the local changes are subtle at best until 60K. At 20K the transformation is complete and the plot is changed, but the shortest distance (Ni to nearest Al) is unchanged while the longer pair distances are split or shifted. This plot is consistent with the 7R crystal structure noted in the literature.

AuZn single crystal shows, figure 5(a), a linear decrease in the elastic constants in the austenite phase and a transformation near 62K. The single crystal shows no sign of the approaching transformation, but the austenite polycrystal (b) “feels” the phase transition and the curvature increases as it approaches. This data from $\text{Ni}_{0.62}\text{Al}_{0.38}$ and AuZn suggests that either the boundary conditions or the crystallite size changes the coupling of the free energy to strain in these martensitic transformations.

These materials by their anomalous dF/dT values suggest an inherent instability that has been associated with the appearance of “tweed”, a reticulated, diffuse pattern in electron microscope images, in the austenite phase prior to and anticipating the formation of the microstructure in the martensite. Tweed is not seen at very high temperatures in the EM, but RUS measurements on NiTi see the anomalous dF/dT values still at greater than 500C, suggesting the lattice may never be stable.

Perovskites

Stripes are also seen in the low temperature phase of the perovskites. However, unlike martensites, there is no precursor behavior beyond expected critical fluctuations, and the driving mechanism is not a shear acting in a weak direction, but a degeneracy raising effect like the Jahn-Teller effect which can be associated with charge or valency redistributions.

RUS measurements show the expected high dissipation in the low temperature phase, and despite this, has gathered some evidence for the existence of another much debated transition in SrTiO_3 at 37K. $\text{La}_{0.83}\text{Sr}_{0.17}\text{MnO}_3$ shows very complex structural and electronic behavior.

The high temperature phase is trigonal, but the distortion is so arranged that RUS sees the global symmetry as cubic. A structural phase transformation changes this to orthorhombic, and the attendant microstructure is shown by an increased dissipation, but the microstructure still averages to cubic in a RUS experiment. Data on this material are published [Publications 1,2].

Modeling

We focused on materials where elasticity plays a crucial role [e.g. as an order parameter (OP) in a solid-solid phase transition]. Our approach to the inherent complexity and collective, multiscale, phenomena was to merge techniques from traditional materials science, statistical physics and nonlinear condensed matter to relate materials texture to local (e.g. electronic or magnetic) functionalities. The elastic strain may be the primary driving force or OP (i.e. proper ferroelastics) such as in martensitic and shape memory alloy: NiTi, FePd, CuAlZn, etc. Strain may also be a secondary OP (i.e. improper ferroelastics) in materials where some other physical property is of prime interest. Examples include (i) magnetoelastics (e.g. Terfenol: $\text{Tb}_x\text{Dy}_{1-x}\text{Fe}_2$ which has the highest known magnetostrictive coefficient) with magnetization as the primary OP, (ii) piezoelectrics, ferroelectrics and antiferroelectrics (BaTiO_3 , SrTiO_3 , PZT which has among the highest known electrostrictive coefficients) usually with polarization as the primary OP, (iii) colossal magnetoresistance (CMR) perovskites ($\text{La}_x\text{Sr}_{1-x}\text{MnO}_3$), and high temperature superconductors (La_xCuO_4 , YBaCuO_7).

In all of the above complex electronic/elastic materials, along with the atomic scale inhomogeneities of charge, spin and lattice distortion, have come observations of "fine-scale structure" on more materials science scales (100s of lattice constants and beyond) through rapid improvements in high-resolution microscopies. These observations of twinning, tweed, etc., appear in extensive precursor regimes of global solid-solid phase transformations or as functions of mechanical stress. This multiscale structure is increasingly understood to produce anomalous elastic constants, low-symmetry lattice vibrations, low-frequency scattering in x-ray and neutron spectra, and inhomogeneous coupling to electronic, magnetic, ferroelectric and superconducting degrees of freedom. The associated multiscale, dynamics is intimately involved in shape-memory, relaxor and related phenomena.

The mechanism by which local perturbations (such as localized charge patterns) can have large-scale effects on elastic patterning is {it anisotropic long-range strain-strain coupling}. This *long-range* coupling arises because of elastic compatibility constraints on the allowed *unit cell* deformations (in the absence of bond-breaking) and is therefore indeed inherited from very *local*, atomic scale, symmetries.

We modeled elasticity and solid-solid phase transformations at the coarse-graining level of a nonlinear Ginzburg-Landau (GL) description, including the compatibility constraint self-consistently. This allows a description of systematic twinning, tweed and other fine-scale hierarchical structures, and is the basis on which we are able to demonstrate nucleation of twinning textures by atomic scale impurity patterns, *i.e. to connect intrinsic multiscale phenomena in solid state physics and materials science*. Our model can predict multiscale elastic textures and their consequences in a unified manner. The stress field, that we considered (due to defects, etc.), can be produced by hole doping into transition-metal-oxides---localized polarons with short-range lattice distortions, and by similar means in other complex electronic materials with significant elastic coupling. Our GL model in 2D consists of (i) a triple-well potential F_0 , as is usual for first order transitions, in the deviatoric strain $OP[\varepsilon = (1/\sqrt{2})(\varepsilon_{xx} - \varepsilon_{yy})]$, (ii) harmonic (linear) elastic energy cost F_{cs} due to the compressional [$e_1 = (1/\sqrt{2})(\varepsilon_{xx} + \varepsilon_{yy})$] and shear ($e_2 = \varepsilon_{xy}$) strain that implicitly depend on the OP through compatibility; (iii) coupling of strain(s) to an external or internal (defect, dislocation) stress; (iv) second and fourth order strain gradient terms F_{grad} that induce multiscale competition; and (v) symmetry-allowed couplings F_{compos} of the (scalar) compositional fluctuations $\tilde{\eta}(r)$ to the OP and its derivatives. The dynamics of the continuous OP is assumed to be of the time dependent GL or relaxational type. The compression-shear (CS) strains $e_1(r)$, $e_2(r)$ are written in terms of the order parameter $\varepsilon(r)$ by solving the elastic compatibility (differential) equation. Below we illustrate key results for a square-to-rectangle transition by including the elastic compatibility constraint both in the crystal bulk and at the surface/interfaces. In fig. 6(a) we show formation of low temperature $T < T_0$ parallel-domain structures with only bulk compatibility included. Note that the structures have the proper 45° orientation, but are not true twins: there is no well defined width scale, however we note the similarity to fig. 1. In fig. 6(b) we depict horizontal twin-like structures with only the surface compatibility term included. Now there is a dominant length scale (twin width) in the system but the 'twins' have rough interfaces and are not properly oriented.

When *both* bulk and surface compatibility terms are included we obtain equally spaced, parallel, and properly oriented twins, as shown in fig. 6(c). The corresponding derived (deviatoric) OP strain field $\tilde{\epsilon}(r)$ in the austenite falls off as 'decaying twins' away from the habit plane, as depicted in fig. 6(d). With variation in system size L , the twin width scales as $W \sim \sqrt{L}$. Thus our model clearly captures the essential physics of twinning in these materials.

Figure 7 (a-c) shows the transformation of textures under gradual cooling, from high temperature austenite, through ('configurational glass') tweed above the transition, to martensitic twins below the transition. In fig. 8 we illustrate the effect of a defect with a "Lorentzian" stress profile. We start with the high-temperature square phase (i.e. austenite) just above the tweed formation temperature. As time proceeds the initial defect (red color) (i) coarsens, (ii) attains a particular size with square/rhombus shape and (iii) nucleates the other variant (blue color) at the four corners of the square. At the next stage (a) the blue variant grows, (ii) the defect (elastically) copies itself at the four edge centers of the initial square and (iii) an anisotropic, long range elastic field builds around the initial defect complex. As time proceeds, this process of self-replicating defect variants continues and a tweed-like pattern is formed. Subsequent coarsening leads to merging of red (rectangular strain) variants with themselves and similarly for the blue (rectangular strain) variants along the diagonal. Eventually the whole system transforms into a twinned martensite (i.e. the low-temperature rectangular phase). One can interpret this process as a stress-induced martensite (caused by the initial defect stress). Branched twins have been observed under dynamic biaxial loading of the shape memory alloy CuAlNi.

Summary:

Positive values of the temperature coefficient of the elastic constants far from a transition is an indicator of lattice instability and a precursor of a martensitic transformation. Tweed may coexist with this condition, but be too subtle for diffraction measurements to detect. A real precursor phase seems to exist in single crystal $\text{Ni}_{0.62}\text{Al}_{0.38}$, which is suppressed by either a size or stress effect in polycrystals, and is not detected in our PDF measurements on powders. AuZn has a martensitic transformation which looks only weakly first order and in fact shares many more features with an order-disorder transformation than with the $\text{Ni}_{0.62}\text{Al}_{0.38}$ transformation, but all show low-T glasslike behavior and unusual dissipation. The tensorial character of the martensite order parameter implies that other non-OP strains are coupled to its variations, through elastic compatibility, generating a Ginzburg-Landau model in terms of the OP strain alone.

At low temperatures, the compatibility-induced anisotropic long-range potential in the bulk and at interfaces, induces equal-width and oriented twins. At higher temperatures, in conjunction with compositional stress, it induces tweed textures. It is clear from the experimental data on martensites that the range of the interaction over which strain deviations can "copy" themselves, and the boundary conditions surrounding the austenite play a critical role in the transformation. The role of disorder in the martensite leading to glass-like behavior at low temperatures has not yet been approached in the modeling, nor the elastic response of the generated structures.

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- [2] Liu, Finlayson, Smith and Tanner, *Mat. Sci. Eng.* **A157** 1992

Figure Captions

Figure 1: HREM picture of martensite microstructure

Figure 2: RUS measurement of a nickel-aluminum alloy at different grain sizes

Figure 3: PDF data on a nickel-aluminum alloy at different temperatures

Figure 4: Low temperature behavior of Ni-Al and an amorphous alloy

Figure 5: "Precursor" behavior in single-crystal and polycrystal AuZn

Figure 6: Generating twin stripes of equal width

Figure 7: Progression from "tweed" in the austenite phase to twins in martensite

Figure 8: Time evolution of the growth of martensite structures

Figure 1

Figure 2

(a)

(b)

Figure 3

(a)

(b)

Figure 4

(a)

(b)

Figure 5

Figure 6 a b
 d c