

MATERIALS SCIENCE

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Magnetism and Structure in Functional Materials

 Springer

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Magnetism and Structure in Functional Materials

With 129 Figures (8 in color)

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Preface

This book is based on the emerging notion that a thorough and fundamental understanding of the interplay of magnetism and structure is needed if a wide variety of functional materials are to be efficiently used in applications. The intent is to foster interaction between researchers in three distinct but related topics: (i) magnetoelastic materials such as magnetic martensites and magnetic shape memory alloys, (ii) magnetocaloric effects related to magnetostructural transitions, and (iii) colossal magnetoresistance (CMR) manganites and related perovskites. The goal is to identify common underlying principles in these three classes of materials that are relevant to optimize various functionalities. The interplay between structure and magnetic properties is sensitive to disorder and manifests itself at multiple length scales in a cross-correlated and hierarchical fashion.

Functional materials are becoming a major theme of the XXI century research. The emergence of apparently different magnetic/structural phenomena in disparate classes of materials (mentioned above) clearly points to a need to integrate common concepts in order to achieve a broader understanding of the interplay between magnetism and structure in this general class of functional materials. This book represents the first steps toward this goal and we hope it reflects this at least in spirit. The idea for this book was born at the workshop *Interplay of Magnetism and Structure in Functional Materials* held at the Benasque Center for Science in the Pyrenees mountains during February, 9–13, 2004.

The topics covered here are interdisciplinary in nature and the chapters are written by expert researchers, who are from physics, materials science, applied mathematics and engineering backgrounds. Therefore, the book is addressed to both the experts and researchers getting into the field of magnetic functional materials including graduate students.

The eleven chapters are arranged as follows. The first two chapters (respectively by Shenoy et al. and Castán et al.) focus on the general aspects of phase transitions in multiferroic materials such as the role of elastic compatibility and long-range interactions, coupling between strain and other impor-

tant physical variables, e.g. magnetization, polarization, orbital ordering, etc., role of disorder in pretransitional phenomena and transition kinetics, local structure probes and phonon anomalies. The next two chapters by Morellon and Ibarra, and by Egami, cover a broad variety of magnetoresistive, magnetostrictive and superconducting materials where the authors discuss the role played by the interplay of spin, charge, orbital and lattice degrees of freedom on their properties. The chapters by Shapiro, Venkateswaran and De Graef, and Brown et al., review and provide exciting new results concerning the anomalous phonon behavior, structural and magnetic precursors and techniques for imaging them. James and Zhang provide an applied mathematical perspective on the problem of martensites as well as the conditions for the coexistence of ferroelectricity and magnetism. The century old (but still not fully understood) problem of the Invar as well as anti-Invar effects are reviewed by Wasserman and Acet. Finally, Pecharsky and Gschneider Jr. and Casanova et al. elaborate on the magnetocaloric effects and emerging new materials and applications. The last chapter by Prof. P.-A. Lindgård nicely summarizes the workshop held in Benasque and provides perspectives for the future.

We would like to dedicate this book to the memory of Prof. James A. Krumhansl who passed away while writing the Introductory chapter. This unfinished chapter with his thoughts on the complex functional materials is also included in the beginning of this book. Over six decades Prof. Krumhansl inspired many generations of scientists in the multidisciplinary field of complex materials and brought the concept of (elastic) solitons in materials science as simply being domain walls or twin boundaries. He also popularized the physicist's notion of phonons among metallurgists which has undoubtedly helped the interpretation of many experimental observations.

Finally, we gratefully acknowledge financial support from MCyT (Spain), AGAUR (Catalonia), University of Barcelona, Los Alamos National Laboratory, the U.S. Department of Energy and Benasque Center for Science. We specially thank Prof. Pere Pascual (Director of Benasque Center) for gracefully providing the conference facilities at Benasque.

Barcelona and Los Alamos,
October 2004

Antoni Planes
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Complex Functional Materials

J.A. Krumhansl

[Based on notes provided by Prof. J.A. Krumhansl to the editors.]

To begin with, I want to say that the idea that complex functional/adaptive materials are a new, recent discovery displays a shallow knowledge of metallurgy, last century's condensed matter physics, and electrical engineering. But to get on to the point of the title: Some ten years ago when many *complex... materials* were being widely publicized for new funding, Dick Slansky, then Director of the Theoretical Division at Los Alamos National Laboratory, was complaining to me: "What good does 'complex', defined as non-simple, do for us scientifically? What kind of a guiding principle for science is that?"

To our great surprise we found that the main definition of "complex" has a well-defined meaning and is very useful to generalize to materials. Simple, we found the answer in most dictionaries! To me it is a most conceptually useful definition, and I hope you find it so too:

Complex (def. 1): "Composed of interconnected or interwoven parts"... This is the main meaning.

And it clearly describes many early Complex Functional Materials, such as a ferromagnet. That early work identified multiple domains which moved at the mesoscopic scale in response to an applied field by motion of magnetic domain walls. The effect is to change the average macroscopic magnetization. So this definition describes an array of interwoven microscopic phases which move, respectively, to change a macroscopic condition. Not surprisingly the same ideas apply to ferroelectrics and ferroelastics (martensites) and shape memory materials. The materials discussed in this book now can also be thought of in this context.

I offer some miscellaneous remarks on modern materials science. An important reference is "Renormalization Group Theory: Its basis and formulation in statistical physics", Michael E. Fisher, *Reviews of Modern Physics* **70**, p. 653 (1998). Read particularly pp. 653–655 and consider the following questions (1) Is the Renormalization Group (RG) a fundamental principle or a calculation method? (2) What fraction of all phase transitions are second order? Is Renormalization Group needed generally in Materials Science? (3) Is there really such a thing as First Principles calculations (at finite temperature)? What

is an effective Hamiltonian in modern condensed matter physics? I provide a few hints and partial answers. A vast majority (more than 90%) of all phase transitions in nature are of first order. Renormalization Group is essentially a calculational procedure. However, the Landau theory is of fundamental importance in materials science and so forth.

The key word for modeling is multiscale. Physically realistic models can start at the mesoscopic scale where the notion of an order parameter and the corresponding Ginzburg–Landau free energy (for phase transitions) are essential. The coefficients of this free energy must be determined from experimental data such as structural, phonon dispersion, and thermodynamic response functions. Alternatively, these coefficients can be determined from microscopic calculations, e.g., electronic structure calculations and molecular dynamics simulations. The single crystal Ginzburg–Landau models can be extended to polycrystals and then suitably coarse grained to serve as input for continuum level constitutive response models.

Over the past half century I have had spirited discussions and shared many ideas with most of the authors in this book, and my own understanding of complex materials and multiferroics, using martensites as a prototypical example, has evolved. Understanding is always a relative word and I believe that the younger generation of scientists will take it to the next level by exploiting the modern tools of computational science, high resolution microscopies, and a suite of characterization techniques. The path to new ideas and applications in the field of functional materials is multidisciplinary – a synergy between metallurgists, materials scientists, physicists, applied mathematicians, engineers, and even biologists. We have to learn a lot from biology in terms of how evolution has optimized biological functionality.

Spin, Charge, and Lattice Coupling in Multiferroic Materials

S.R. Shenoy, T. Lookman, and A. Saxena

2.1 Introduction

Functional materials are those with technologically useful properties that can be sensitively controlled by external parameters. The need to understand and to use functionalities of shape memory alloys, relaxor ferroelectrics, colossal magnetoresistance manganites, superconducting cuprates and other materials, is one motivation for their intense current study [1–11]. Of course, applied stress, magnetic field or voltage will, respectively, induce *direct-variable* changes in strain, magnetization and electric polarization. More interestingly, in multifunctional materials with mutually coupled variables, there is also a *cross-variable* response, so a given field could control two or more variables, or a variable can be switched by two or more external fields.

Thus in magnetic shape memory alloys, with coupled strain and magnetization, the external shape can be controlled both by pressure and by magnetic field; and stress changes magnetization, while magnetic field affects structure [12]. In colossal magnetoresistance manganites [3], the conductance (that is related to magnetization), rises by many orders of magnitude in response to uniform magnetic fields as well as to hydrostatic pressure; while voltage induces changes in local structure and conductance [13, 14]. In ferroelectric manganites, polarization can be switched by a magnetic field [15]. In cuprates [7] the superconductivity is suppressed as usual by a magnetic field, but is also controlled by stress [16]; shape memory-like effects can occur [17]; and surprisingly (for these doped antiferromagnets), an external uniform magnetic field can rotate elastic domain walls [18]. Thus a variety of materials show cross-variable response in their macroscopic multifunctionalities, implying strong coupling of magnetic spin, electronic charge and lattice strain.

Finescale local probes have revealed something surprising, however. Many transition metal oxides spontaneously form *nonuniform* complex patterns of charge, spin and strain variables at scales of a nanometer and upwards [4–6, 19–26]. The multivariable patterning includes structural stripes,

magnetic droplets and conducting filaments, and there has been much experimental and theoretical interest in this “nanoscale phase separation” or “intrinsic heterogeneity” [4–6]. There is also a remarkable *cross-scale* response: a uniform or *macroscale* magnetic field can induce *mesoscale* structural changes, or *nanoscale* conductance variations [18, 19].

An understanding of these multiscale, multivariable textures is crucial to tailoring multifunctionalities on the macroscale [10]. Clearly, a uniform order parameter (OP) Landau model is insufficient. The *spatially varying* patterns of charge, magnetization, and strain must emerge as the locally stable minimum of some multivariable, nonlinear, free energy functional.

Spatial variation as a preferred state is not new, of course. Purely ferroelastic materials with a *strain tensor* order parameter, such as shape memory alloys like FePd, show mesoscale “twins” or bands of coexisting unit-cell variants, below the structural transition [27]; or woolen-fabric-like “tweed” of oriented criss-cross striations on a finer nanoscale, above the transition [28]. In martensites, interfaces can also be dynamic, with acoustic emission on quenching, from domains advancing at sound speeds [29]. Superconducting cuprates are also doped ferroelastics [30], and show both twinning and tweed, as emphasized by Krumhansl [7]. Magneto-resistant metallic glasses exhibit mesoscale tweed [31]. Relaxor ferroelectrics/magnetoelastics also show twins and tweed in electric polarization/magnetization [12, 32].

The similarity and ubiquity of textures in very different materials prompts a search for a common link. Competition between short- and long-range forces, and/or sign-varying frustration effects are known to generically favour patterning [33]. Since all variables live on a discrete, d -dimensional crystal lattice, it follows that local deformation or strain of the lattice both affects spin and charge, and in turn is influenced by them. It turns out that in ferroelastics, generic lattice-integrity *constraints* on the $\frac{1}{2}d(d+1)$ components of the symmetric strain tensor [34] can induce effective long-range interaction *potentials*, with sign-varying angular variation, and power-law decay. Working in a strain representation, rather than in the more conventional displacement representation, reveals these hidden, texture-inducing correlations. The origins of intrinsic inhomogeneities could lie in the ubiquitous strain tensor: its power-law interaction, its nonlinearity, and its coupling to other variables.

We focus on this emerging viewpoint [35–42], without giving a proper review of other approaches, or any more than illustrative references. In Sect. 2.2 we consider coupled “multiferroic” order parameters. Section 2.3 discusses the St Venant compatibility constraint that induces the effective long-range potential. Intrinsic inhomogeneities in proper ferroelastics and multiferroic oxides, are discussed in Sects. 2.4 and 2.5, respectively. Section 2.6 outlines the modelling of oxides, with charge and spin acting as local stresses and temperatures. A summary, with speculations on further work, is given in Sect. 2.7.

2.2 Order Parameters and Multiferroics

The order parameter is a basic concept in phase transitions [43]: a variable whose thermal average becomes nonzero below a transition temperature or pressure either continuously (second-order) or discontinuously (first-order). The free energy lowering can involve a global dominance of a uniform state: only one out of N_V competing, lower symmetry, degenerate minima or “variants” is finally present. Nonlinearity of the free energy functional in such second order transitions is manifest close to the transition, where renormalizations occur due to nonuniform critical fluctuations of competing variants.

Structural phase transitions involve a change in the discrete symmetry of the unit cell, with lattice points shifting on cooling (or application of stress) to new lower-symmetry positions. Ferroelastic displacive structural transitions [1] are those for which the symmetry of the low-temperature unit cell is a *subgroup* of the high-temperature unit cell symmetry. The order parameters (OP) for first-order ferroelastic transitions are $N_{OP} \leq d$ independent components of the strain tensor, that can exhibit strain hysteresis under applied stress. The free energy lowering can involve a global coexistence of nonuniform states: all the N_V lower symmetry variants are finally present. Nonlinearity of the free energy functional in such first-order transitions is manifest for temperatures all the way below, and for a range above, the transition. Structural static domain walls such as in twins or tweed, and dynamic excitations, are elastic solitons [27,28,44], and the nonuniformity is a signature of nonlinearity.

Domains and hysteretic switching occur, of course, in several types of materials – indeed the very name “ferroelastic” and “ferroelectric” derive from the analogy with ferromagnets: they all have such behaviour in common (but not the element of Fe, ironically!) These three materials classes can be grouped under the common rubric of “ferroics” as they all “undergo nondisruptive phase transitions that alter their point group symmetry” with strain, electric polarization, or magnetization as the respective order parameters [9]. Materials with two or more ferroic OPs, and a sequence of nested phase transitions, are *multiferroics*, that can have mutually *coupled nonlinearities*. A primary order parameter at its transition temperature (or composition), can drive the other, secondary OPs; with roles exchanged at the other, nested transitions. For example cuprates have a ferroelastic structural transition [30], with strain as the primary OP, that can be followed on cooling by a Néel transition, with staggered magnetization as the primary OP [7]. In manganites depending on the doping, there is a complex phase diagram, with ferromagnetic, charge-order, ferroelastic and Jahn-Teller transitions [3,6].

As illustrated in later sections, cuprates and manganites could be regarded as examples of *complex* multiferroics in the sense of Krumhansl, who speaks in this volume of complex materials as composed of interconnected parts, with interwoven microscopic phases moving relatively, to change a macroscopic condition. This picture of annealed-variable texturing

is complementary to quenched-disorder effects, certainly also present [6]. The multiferroic conceptual umbrella, and an approach that studies cuprates in the context of manganites and other oxides [23], might have pleased Krumhansl, who also remarked that “by and large, the physics literature on high T_c seems to be unfortunately disjoint from much earlier work on displacive phase transitions, or other areas of materials science, notably ferroelectricity and metallurgy” [7].

2.3 Strain Tensor and Elastic Compatibility

In this section we focus on “proper” ferroelastics that have only a strain tensor order parameter [1] and later consider couplings to other variables, in “improper” ferroelastics. Suppose we only consider those deformations of the crystal lattice that do not create dislocations and vacancies. Then the central point is that this seemingly innocuous “no-defect” constraint, of lattice integrity maintained at every instant, implies the existence of anisotropic, power-law (APL) correlations between order-parameter strains.

2.3.1 Levels of Description

The unit cell sets the minimum scale for strain variations. More generally, it is useful to define levels of description for probe distances R , as in Fig. 2.1. *Level 0* or $L_0 \sim R \gg a_0$ (lattice constant) is the macroscopic regime of engineering strains, and of system size and shape. *Level 1* is the regime of unit-cell strains, that can have meso- and nanoscale variations within the large range $L_0 > R > a_0$. The intracell regime of *Level 2* involves the bond angles and lengths, $a_0 > R \sim \ell_0$, of the atomic basis whose deformation

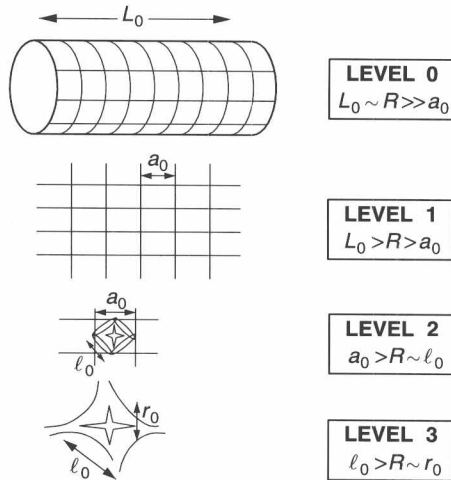


Fig. 2.1. Levels of description. See text, Sect. 2.3.1

may be termed as the “microstrain”, e.g. Jahn–Teller-like distortions of perovskite octahedra [21]. Finally, *Level 3* is the Ångstrom-scale regime of the electron occupancies/spin states of individual-atom wavefunctions on scales $\ell_0 > R \sim r_0$, e.g. *d*-wave orbitals or core spins. Of course, the levels are coupled. The Level 1/Level 2 interface is where the elastic physics meets the structural chemistry. Jahn–Teller Hamiltonians [3] link Level 3 orbital occupancies to Level 2 octahedral “ Q_2, Q_3 ” stretchings; these in turn represent Level 1 unit-cell strain distortions.

The material specifics of the multiferroics are in the detailed nature of the charge/polarization/spin variables; their symmetry-dictated couplings to each other and to strains; and the values and signs of the coupling constants as well as energy scales. But for materials with strong elastic anisotropy (from directional Level 2 bonding, or basis atoms with widely different sizes), the common key is the Level 1 strain. Its APL elastic correlations, nonlinearities, and couplings to other variables, could possibly induce domain-wall patterned states, as local minima of a multivalley free energy landscape. The power-law correlations are in a certain sense, scale-free, and could link widely separated variables at finer levels of description.

2.3.2 Definition of Unit-Cell Strain Tensor

Engineering strain is a Level 0 description of distortions of a medium, with derivatives of a continuous displacement $\mathbf{u}(\mathbf{r}')$, labelled by a continuum position \mathbf{r}' [43,45]. On the other hand, unit-cell strain in a crystal lattice with lattice points \mathbf{r}_i can be defined as a Level 1 continuous variable, that is a *discrete difference* of lattice-point displacements $\mathbf{u}(\mathbf{r}_i)$. It reduces to macroscopically varying engineering strains in the continuum limit of lattice constant $a_0 \rightarrow 0$, when the discrete differences become derivatives. Consider for simplicity, a cubic lattice with atoms at lattice points \mathbf{r}_i (scaled in a_0) interacting through a two-body potential V that depends only on the magnitude of their separation $\mathbf{r}_{i,j} = \mathbf{r}_i - \mathbf{r}_j$. Then for a deformed lattice with points at $\mathbf{R}_i = \mathbf{r}_i + \mathbf{u}(\mathbf{r}_i)$, the energy change $\Delta V = V(|\mathbf{R}_{i,j}|) - V(|\mathbf{r}_{i,j}|)$ is

$$\Delta V = V(|\mathbf{r}_{i,j} + \mathbf{u}(\mathbf{r}_i) - \mathbf{u}(\mathbf{r}_j)|) - V(|\mathbf{r}_{i,j}|). \quad (2.1)$$

For nearest-neighbour lattice points, $\mathbf{r}_i = \mathbf{r}_j + \hat{\mu}$ (where $\hat{\mu} = \hat{x}, \hat{y}, \hat{z}$) the discrete difference [46] of the displacement-vector components naturally appears, $\Delta_\mu u_\nu(\mathbf{r}_j) \equiv u_\nu(\mathbf{r}_j + \hat{\mu}) - u_\nu(\mathbf{r}_j)$. More specifically, in changes of the squared separations

$$|\mathbf{R}_{j+\hat{x},j}|^2 - |\mathbf{r}_{j+\hat{x},j}|^2 = 2E_{xx}, \quad (2.2)$$

the differences appear as $\frac{1}{2}d(d+1)$ components of a unit-cell, symmetric strain tensor that is *defined* by

$$E_{\mu\nu} \equiv \frac{1}{2} [\Delta_\mu u_\nu(\mathbf{r}_i) + \Delta_\nu u_\mu(\mathbf{r}_i) + G_{\mu\nu}]. \quad (2.3)$$