Crystals, Defects and Microstructures

Modeling Across Scales

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ONE

Idealizing Material Response

1.1 A Material World

Steel glows while being processed, aluminum does not. Red lasers are commonplace, while at the time of this writing, the drive to attain bright blue light is being hotly contested with the advent of a new generation of nitride materials. Whether we consider the metal and concrete structures that fill our cities or the optical fibers that link them, materials form the very backdrop against which our technological world unfolds. What is more, ingenious materials have been a central part of our increasing technological and scientific sophistication from the moment man took up tools in hand, playing a role in historic periods spanning from the Bronze Age to the Information Age.

From the heterostructures that make possible the use of exotic electronic states in optoelectronic devices to the application of shape memory alloys as filters for blood clots, the inception of novel materials is a central part of modern invention. While in the nineteenth century, invention was acknowledged through the celebrity of inventors like Nikola Tesla, it has become such a constant part of everyday life that inventors have been thrust into anonymity and we are faced daily with the temptation to forget to what incredible levels of advancement man's use of materials has been taken. Part of the challenge that attends these novel and sophisticated uses of materials is that of constructing reliable insights into the origins of the properties that make them attractive. The aim of the present chapter is to examine the intellectual constructs that have been put forth to characterize material response, and to take a first look at the types of models that have been advanced to explain this response.

1.1.1 Materials: A Databook Perspective

What is a material? The answer to this seemingly nonsensical question strikes right to the heart of some of the key issues it is the aim of this book to examine.

From the most naive of perspectives, questions surrounding the defining qualities of a particular material are easily answered in terms of our everyday perceptions: weight, luster, color, hardness, susceptibility to heating. However, these simple notions are a reflection of a deeper underlying identity, an identity that is revealed quantitatively the moment one poses the question of precisely how a given material replies when affected by some external probe. If we subject a material to a force, it changes shape. If we apply a potential difference, electrical current might flow. And if the temperatures of the two ends of a sample are different, a flow of heat results. In each of these cases, these experiments reveal something further about the identity of the material in question.

One of the overarching conceptual themes that has emerged from such simple experiments and that rests behind the quantitative description of materials is the idea of a material parameter. For example, Hooke's original efforts, which were aimed at uncovering the relation between a body's extension and the applied force that engendered it, led to the recognition that there exist a series of numbers, namely the elastic moduli, that characterize the elastic response of that material under different loading conditions. Similarly, there is a well established tradition of subjecting materials to applied fields which result in the emergence of various fluxes such as the electrical and thermal currents mentioned above. Allied with these fluxes are material parameters that link the response (i.e. the flux) to the applied field. In these cases and many more, the central idea is that a particular material can be identified in terms of the specific values adopted by its material parameters. In fact, for some purposes, a particular material may be idealized completely in terms of a set of such parameters. For the elastician, single crystal Al is characterized by a density and three elastic constants, namely, $C_{11} = 106.78$ GPa, $C_{12} = 60.74$ GPa and $C_{44} = 28.21$ GPa (data for Al at 300 K taken from Simmons and Wang (1971)). By way of contrast, to the engineer concerned with the application of Al in thermal environments, Al is specified in terms of a density and a thermal conductivity $\kappa = 2.37$ W/(cm K) (data for Al at 300 K taken from Shackelford *et al.* (1995)). This type of idealization of a material in which its entire identity is represented by but a few numbers is one of far-reaching subtlety. In the context of the elastic constants, all of the relevant atomic bond stretching and bending has been subsumed into the three material parameters introduced above. Similarly, the full complexity of the scattering of phonons giving rise to the thermal properties of a material has also been subsumed into just one or a few numbers. One of our primary missions in the coming chapters will be to explore how such effective theories of material behavior may be built strictly on the basis of such material parameters and to examine what gives rise to the difference in these parameters from one material to the next.

From the standpoint of the idea given above, a particular material is characterized by a set of numbers that can be unearthed in a databook. For example, important parameters include the density ρ, the yield stress σ_y, the fracture toughness K_{IC} and the diffusion constant D. We note that in each case there is a number that can be looked up that characterizes the weight of a material in some normalized terms (i.e. the density), the resistance of the material to permanent deformation and fracture (yield strength and toughness), the ease with which mass can be transported within the material at elevated temperatures (diffusion constant) and any of a number of other possibilities. Our main point is to illustrate the way in which a given number (or set of numbers) can be used to introduce material specificity into continuum treatments of material response. For example, in considering the continuum treatment of mass transport, it is held that the flux of mass is proportional to the gradient in concentration, with the constant of proportionality being the diffusion constant. This same basic strategy is exploited repeatedly and always hinges on the fact that the complexity of the atomic-level processes characterizing a given phenomenon can be replaced with a surrogate in the form of material parameters.

The significance of the notion of a material parameter is further clarified by putting the properties of different materials into juxtaposition with one another. In figs. 1.1 and 1.2, we follow Ashby (1989) with some representative examples of the range of values taken on by a few prominent material properties, namely the Young's modulus, the yield strength, the fracture toughness and the thermal conductivity. The basic idea adopted in Ashby's approach is to allow the contrasts between the properties of different materials to speak for themselves. One of our aims in the chapters that follow will be to develop plausible explanations for the range of data indicated schematically in fig. 1.1, with special attention reserved for thermomechanical properties.

Despite the power of the idea of a material parameter, it must be greeted with caution. For many features of materials, certain 'properties' are not *intrinsic*. For example, both the yield strength and fracture toughness of a material depend upon its internal constitution. That is, the measured material response can depend upon microstructural features such as the grain size, the porosity, etc. Depending upon the extent to which the material has been subjected to prior working and annealing, these properties can vary considerably. Even a seemingly elementary property such as the density can depend significantly upon that material's life history. For a material such as tungsten which is often processed using the techniques of powder metallurgy, the density depends strongly upon the processing history. The significance of the types of observations given above is the realization that many material properties depend upon more than just the identity of the particular atomic constituents that make up that material. Indeed, one of our central themes will

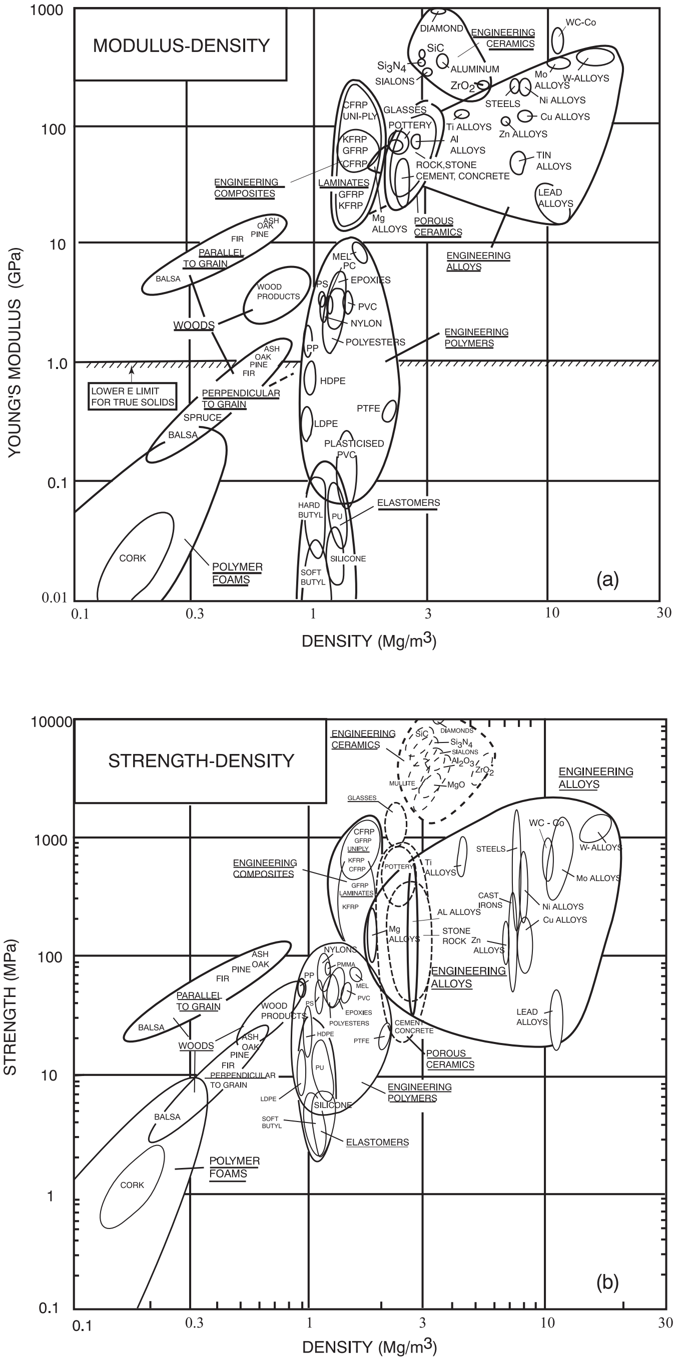

Fig. 1.1. Elastic and plastic properties of a wide class of materials (adapted from Ashby (1989)).

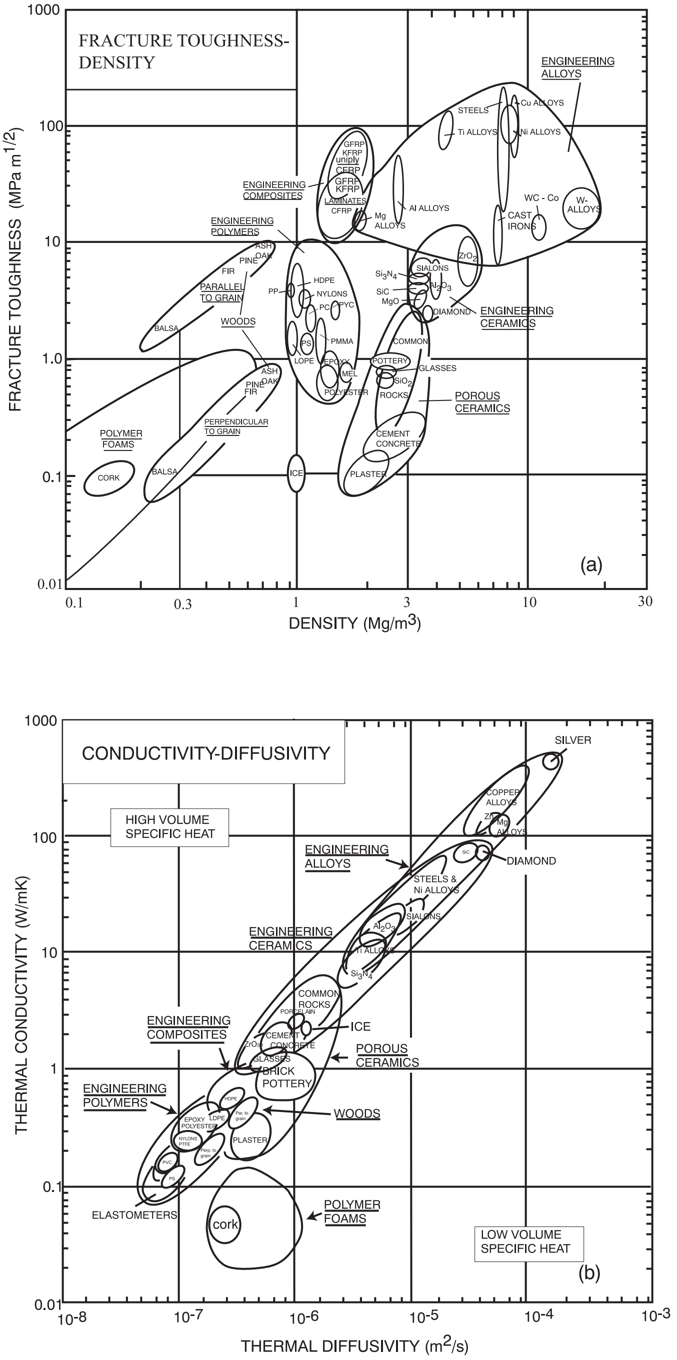

Fig. 1.2. Fracture and thermal properties of a wide class of materials (adapted from Ashby (1989)).

be the argument that microstructural features such as point defects, dislocations and grain boundaries can each alter the measured macroscopic ‘properties’ of a material.

One of our primary concerns in the pages that follow is to understand the emergence of material properties on the basis of the geometric structures that populate materials. This critical link between structure and properties has been canonized through the structure–properties paradigm which elevates the analysis of structure as a prerequisite to understanding properties. We have tried, in this section, to present something of the backdrop against which we will develop models of material behavior, especially with reference to thermomechanical properties. As an introduction to such models we first examine the role played by geometric structure in dictating material properties, followed by an overview of the ways in which materials may be tailored to yield particular values of these material parameters.

1.1.2 The Structure–Properties Paradigm

In the previous section we noted that, in the abstract, Al (or any other material) may be characterized by a series of numbers, its material parameters, to be found in a databook. However, as we already hinted at, because of the history dependence of material properties, the description of such properties is entirely more subtle. There is no one aluminum, nor one steel, nor one zirconia. Depending upon the thermomechanical history of a material, properties ranging from the yield strength to the thermal and electrical conductivity can be completely altered. The simplest explanation for this variability is the fact that different thermomechanical histories result in different internal structures.

A fundamental tenet of materials science hinted at in the discussion above is the structure–properties paradigm. The claim is that by virtue of a material’s structure many of its associated properties are determined. Structure is an intrinsically geometric notion and one of the abiding themes in this book will be the constant reminder that it is structure on a variety of different length scales that gives rise to many of the well-known properties of materials. From the atomic-scale perspective we will constantly return to the implications of the fact that a material has a given crystal structure, whether it be for its role in dictating the properties of interfacial defects such as antiphase boundaries or the elastic anisotropy that must enter elasticity theory if the crystal symmetries are to be properly accounted for. Next, we will devote repeated attention to the lattice defects that disturb the uninterrupted monotony of the perfect crystal. Vacancies, interstitials, dislocations, stacking faults, grain boundaries and cracks will each claim centerstage in turn. At yet lower resolution, it is geometry at the microstructural scale that comes into relief and will occupy much of our attention. At each of these scales we will return to

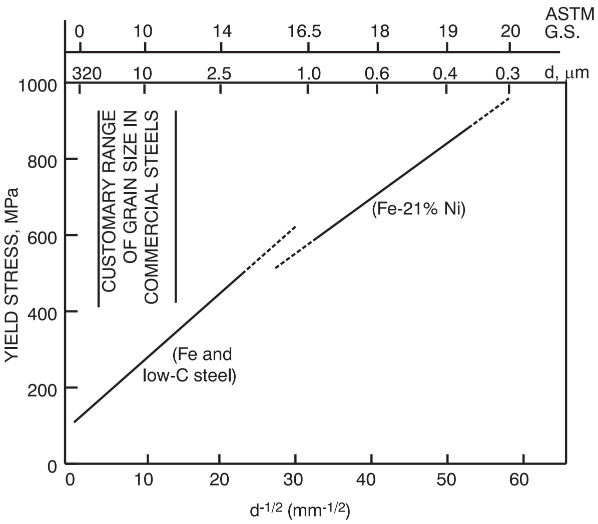

Fig. 1.3. Yield strength data for steel as a function of grain size *d* (adapted from Leslie (1981)). Plot shows dependence of yield stress on inverse power of grain size. The legends at the top of the figure show the actual grain size as measured in both μm and using the ASTM units for grain size.

the question of the structure–properties paradigm, always with a critical eye, to see just how far it may take us in our desire to unearth the behavior of real materials.

A celebrated example of the coupling of structure and properties is exhibited in fig. 1.3 in which the relation between the yield strength and the grain size is depicted. In particular, the Hall–Petch relation posits a relation between the yield stress and the grain size of the form $\sigma_y \propto 1/\sqrt{d}$, where d is the grain size of the material. The Hall–Petch relation leads us to two of the most important notions to be found in contemplating materials: the existence of microstructure and its implications for material properties, and the development of scaling laws for characterizing material response. An immediate consequence of the results depicted here is the insight that not only are structures at the atomic scale important, but so too are the geometric structures found at the microstructural scale.

We have noted that the attempt to understand materials demands that we confront a hierarchy of geometric structures, starting with the atomic-level geometries presented by the crystal lattice and increasing in scale to the level of the isolated defects that exist within materials to their assembly into the material's microstructure itself. The quest to understand the structure of a given material inevitably commences with the phase diagram. Phase diagrams are one of the primary road maps of the materials scientist. Such diagrams represent a summary of a series of tedious analyses aimed at determining the *equilibrium* atomic-scale structure of a given element or mixture of elements for a series of temperatures (and possibly

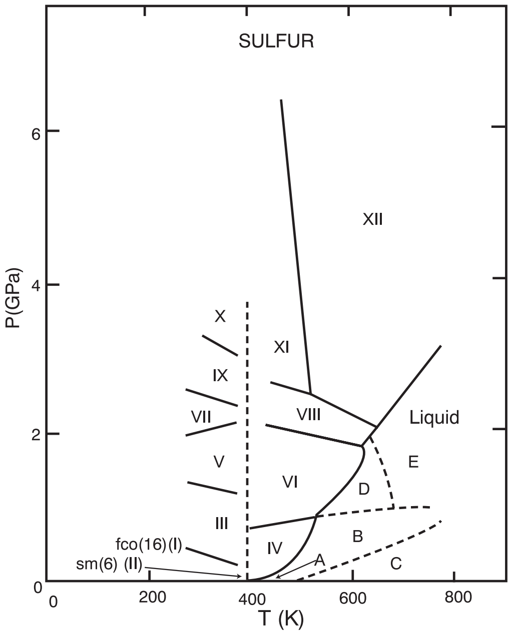

Fig. 1.4. Phase diagram of elemental sulfur (adapted from Young (1991)).

pressures). In figs. 1.4 and 1.5, we show the equilibrium phase diagrams of elemental sulfur and the iron–carbon system. The particular choices of materials shown here are meant to give a feel for the existence of the rich atomic-level complexity that is found in both elemental systems and their alloy counterparts. Note that in the case of elemental sulfur, there are not less than ten different equilibrium structures corresponding to different values of the temperature and pressure. These structures are built around molecular S_8 and range from orthorhombic to monoclinic lattices. The iron–carbon phase diagram illustrates a similar structural diversity, with each phase boundary separating distinct structural outcomes.

Phase diagrams like those discussed above have as their primary mission a succinct description of the *atomic-level* geometries that are adopted by a given system. However, as we have already mentioned, there is structure to be found on many different length scales, and one of the surprises of deeper reflection is the realization that despite the fact that phase diagrams reflect the equilibrium state of a given material, they can even instruct us concerning the *metastable* microstructures that occur at larger scales. The simplest example of such thinking is that associated with precipitation reactions in which an overabundance of substitutional impurities is frozen into a system by quenching from high temperatures. If the material is subsequently annealed, the phase diagram leads us to expect a two-phase

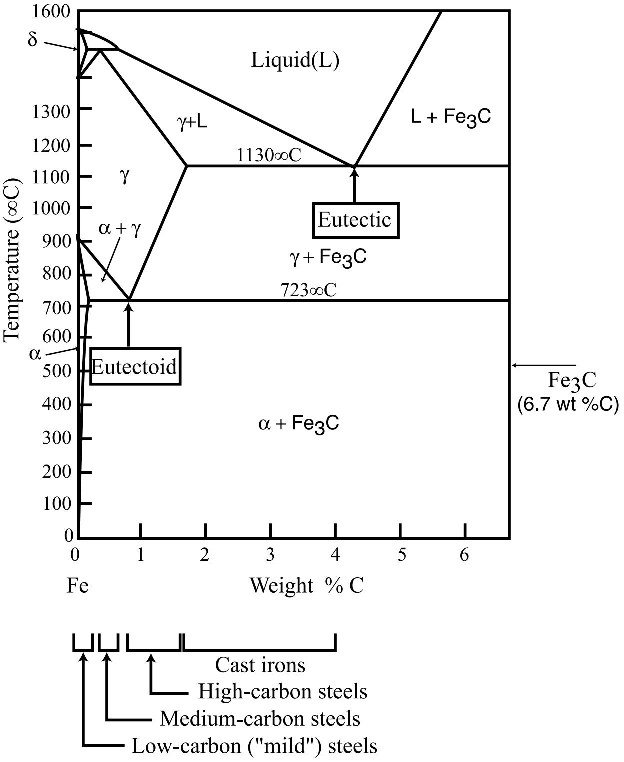

Fig. 1.5. Phase diagram for the iron–carbon system (adapted from Ashby and Jones (1986)).

microstructure in which the overabundance of substitutional impurities is now taken up in the relevant equilibrium phase. What this suggests is that strategies can be concocted for preparing particular metastable states with desirable properties. It is this insight that has led to many of the heat and beat strategies that have attracted pejorative attention to the materials engineer. A broad description of the significance of phase diagrams to materials science may be found in Massalski (1989).

As noted above, the phase diagram instructs our intuitions concerning the atomic-level geometries of materials. At the next level of geometric complexity in the hierarchy of structures that exist within a material, we must confront the defects that populate materials. Indeed, one of the key realizations that we will revisit from a number of different perspectives is that of the role of defects in the determination of material response. What this means is that the structure–properties paradigm makes an ambiguous use of the word ‘structure’ since in different situations, the structures being referenced can range all the way from atomic-scale structure to that of the nature of the grains making up a polycrystal. At the level of the defect geometries found within materials, our present argument is that if we trace yield in crystals to the mechanisms which engender it for example, it is the motion of dislocations which will be implicated. Similarly, if we pursue the stress–strain curve to its limits, the material will fail either through crack propagation or void coalescence or some other defect mechanism. The implication of this insight is that much of the work of modeling the thermomechanical behavior of materials can be reduced to that of carrying out the structure–properties linkage at the level of defect structures within materials.

In later chapters, we will adopt a hierarchical approach to constructing models of material response. First, we will examine the way in which atomistic models can be used to uncover the structural rearrangements in defect ‘cores’ which are a signature of the nonlinear interatomic interactions that are difficult to capture within continuum theory. Once these tools are in hand, we will turn to an analysis of the dominant defect types themselves, with a classification scheme centered on the dimensionality of these defects. Having successfully captured the structure and energetics of single defects, our next mission will be to understand the role of defects as conspiratorial partners in the emergence of observed macroscopic behavior. The uncovering of this conspiracy will in the end always lead us to questions of averaging. The challenge here is in forging the connection between the behavior of single defects, on one hand, and the macroscopic material response, on the other, which often emerges as a synthetic response of many defects in concert.

1.1.3 Controlling Structure: The World of Heat and Beat

In the previous section we considered the critical role played by structures at a number of different scales in determining material properties. From the standpoint of the materials engineer this insight may be recast as a challenge: how may the various structures within a material be tailored so as to yield desired properties? Metallurgy has a longstanding reputation as an empirical subject founded upon the twin pillars of heating and beating a material to some desired form. Whether one resorts to cold working a material or subjecting it to a high-temperature anneal, the outcome of these *processes* is a change in the internal constitution of that material at one or more scales. Because of these structural changes, there is a concomitant change in the properties of the material. Indeed, these strategies for altering the structure of materials should be seen as the answer to the challenge posed above.

By carefully selecting the thermal and mechanical history of a material, it is possible to tailor a number of different features of that material. Low-temperature anneals can induce precipitate reactions that increase the yield stress. Cold working changes the dislocation density, and this too alters the yield stress. If the material

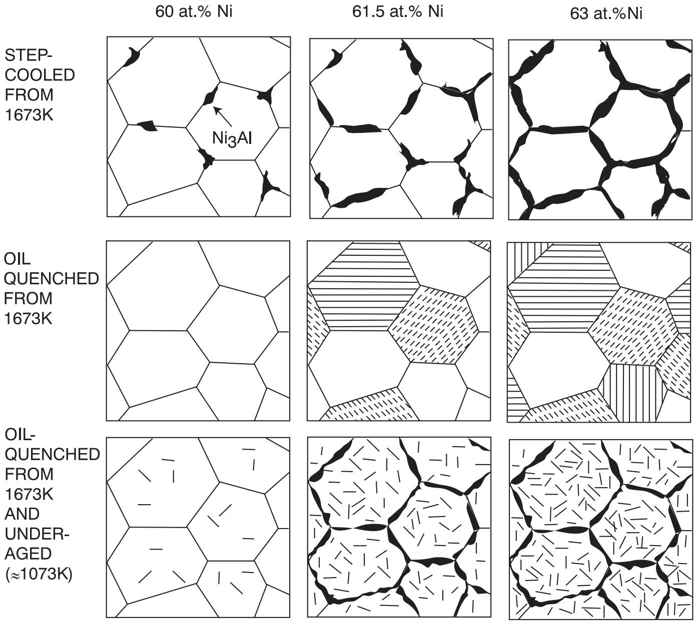

Fig. 1.6. Schematic of the different microstructures for the Ni–Al system that are obtained using different thermomechanical processing schedules (adapted from Kumar *et al.* (1992)). The figure illustrates precipitation at grain boundaries and within grains.

is exposed to a particular chemical atmosphere it can result in a thin surface layer that can increase the material's hardness, a strategy that is adopted in the production of carburized steels. In each of these examples, through annealing (heat) or deformation (beat) or both, the internal structures within the material are changed and as a result, so too are the macroscopic properties.

As an explicit example of how a material changes when subjected to the type of processing program introduced above, fig. 1.6 shows a schematic of the microstructures that arise from slightly different chemical compositions and for different thermal histories for Ni-rich Ni–Al alloys. The figure illustrates the significant variety in microstructure as a function both of slight ($<3\%$) changes in chemical composition and in the aging process. As a result of the aging process, second-phase particles of either Ni_3Al or Ni_5Al_3 can develop. In addition, if the sample is initially slow cooled, Ni_3Al precipitates at grain boundaries, while quenching and subsequent aging induces precipitation in the matrix. As is also indicated in the figure in the striped regions in the middle row, another microstructural outcome is the development of Ni–Al martensite. Out of the series of specimens indicated schematically in the figure, each of which had a different microstructure, the fracture toughnesses varied by as much as nearly a factor of

2. The role of this example in the current discussion is twofold: first, we wish to illustrate the significant structural differences that attend different processing schedules, and second, we aim to show the inextricable link between measured properties and structural features at the microstructural level.

The richness of the microstructures that result from different thermomechanical processing histories is perhaps best illustrated through the example of steels. As was indicated in fig. 1.5, at temperatures below roughly 720 °C, the equilibrium constitution of an Fe–C alloy in the low carbon concentration limit is a two-phase alloy consisting of both α-Fe (ferrite, in the bcc structure) and Fe_3C. However, this description merely tells us which crystal structures are present. The microstructure that attends the presence of these structures is known as pearlite and consists of alternating plates of α-Fe and Fe_3C. For the purposes of the present discussion we wish to note that there are a wide variety of metastable microstructures that can be attained which feature the different phases revealed in the phase diagram. For further details the reader is urged to consult Ashby and Jones (1986) or Honeycombe and Bhadeshia (1995).

In this first section of the book, our intention has been to illustrate the abstract representation of materials by different material parameters and to show how via the structure–properties linkage, material properties can be tuned by controlling the structures themselves. From a quantitative viewpoint, material response is characterized in terms of a series of material parameters that we have argued depend heavily on the internal constitution of materials at a number of different scales. These internal structures can be controlled by a number of different processing strategies. This series of insights now leaves us with the main substance of the type of questions that must be tackled in constructing viable models of material response.

1.2 Modeling of Materials

1.2.1 The Case for Modeling

Modeling has quietly become a ubiquitous part of daily life. Each evening's weather forecast leans heavily on the existence of well-defined theoretical models that are built around the vast quantities of data that are recorded at worldwide weather stations each day. Wall Street thrives on the existence of financial derivatives based largely on stochastic models of pricing and value. In the manufacturing arena, the release of the Boeing 777 exemplifies a reliance on modeling heretofore unknown: structural mechanics and aerodynamics, flight dynamics, operations research, process modeling, modeling of manufacturing, all were part of this huge project. Modeling has assumed an increasingly important role in the materials context as well.

The role of modeling in the materials setting is quite diverse. On the one hand, in the design process, the uses to which materials will be put must be evaluated critically with an eye to performance, reliability and safety. In addition, modeling can play a role in the quest to control materials and the processes used to produce them. At the most fundamental level (and the primary focus of the present work), modeling serves as the basis for an understanding of materials and their response to external stimuli. Broadly speaking, the demands placed on a model strongly depend upon its intended use. Bronze Age practitioners were successful in their material choices without detailed understanding. The challenge of modern alloy design, by way of contrast, is to see if the quantitative understanding from the modern theory of defects may be used to suggest new material strategies. On the one hand, phenomenological models may be entirely satisfactory if the goal is to test the response of a given material to casting in different shapes, for example. On the other hand, if the goal is to produce mechanistic understanding with allied predictive power a phenomenological model may not suffice and might be replaced by detailed insights concerning the underlying mechanisms. From the perspective of the engineer, the pinnacle of the modeling approach is the ability to alter engineering strategies through either the design of new materials or the institution of new processes for exploiting existing materials.

From the perspective of understanding why materials are the way they are, two of the most compelling examples that can be given concern the deformation and ultimate failure of solids. Though we will take up both of these issues again later from a quantitative perspective, our present aim is to illustrate the conceptual leap in understanding that attended the solution to the puzzles of plastic deformation and fracture. The simplest models of both of these processes consider homogeneous solids. In the case of plasticity, deformation was first posited to result from the uniform sliding of adjacent crystal planes, while fracture was envisaged to arise from a similar homogeneous process in which adjacent planes are uniformly separated. The problem with these simple models is that they lead to critical stresses for these processes that are well in excess of those observed experimentally. In both cases, the resolution of the paradox came from modeling insights concerning the role of defects in reducing the critical stresses for these processes. In the case of plastic deformation, the introduction of the dislocation resolved the discrepancy, while in the case of fracture, it was the presumed presence of preexisting cracks.

1.2.2 Modeling Defined: Contrasting Perspectives

As is perhaps already evident, the idea conveyed by the word ‘modeling’ is ambiguous. This ambiguity is ultimately linked to fundamental questions concerning the aims of science itself. At the most fundamental level, there is an age old debate concerning the true object of science: are we describing some underlying reality in nature, or rather is the aim to elucidate rules that yield successively better approximations to what we observe in the world around us? From the latter perspective, even the elaboration of Maxwell's equations or the edifice of classical thermodynamics might be seen as profound exercises in modeling. These types of advances must be contrasted with those in which it is clear from the outset that what is being done is picking off some fundamental feature of what has been observed and casting it in mathematically tractable terms with the aim of making falsifiable predictions.

These arguments are perhaps best illustrated by recourse to examples which serve to demonstrate the ways in which fundamental laws must be supplemented by models of material response. Whether we discuss the electromagnetically busy vacuum of interplanetary space, the absorption of radiation by an insulator or the ceramic innards of a capacitor, our expectation is that Maxwell's equations are the appropriate theoretical description of the underlying electromagnetic response. This part of the 'modeling' process was finished in the last century. On the other hand, the description in terms of these equations alone is incomplete and must be supplemented by constitutive insights which provide a description of the electromagnetic *properties* of the medium itself. In this context we refer to quantities such as the dielectric constant and the magnetic susceptibility. For example, with reference to optical absorption, the classical model of Lorentz assumed that the charges within a material could be thought of as tiny harmonic oscillators with a particular natural frequency. The electromagnetic field impinging on the material has the effect of forcing these oscillators, with the result that one can determine the absorption as a function of incident frequency. Note the character of this model. It is noncommittal with respect to any *fundamental* description of the material. Rather, it aims to reflect some element of the reality of the material in a way that can be calculated and compared with experiment, and, if successful, used as the basis of design.

As another example, this time drawn from the realm of classical thermodynamics, we may consider the thermal state of a neutron star, a high-temperature superconductor or a dense gas. In each case, there is little doubt as to the validity of thermodynamics itself. On the other hand, if we wish to make progress in the description of the dense gas, for example, the laws of thermodynamics by themselves do not suffice. This is where modeling in the sense that it will be used primarily in this book comes in. In addition to the fundamental laws that apply to *all* thermodynamic systems, we must characterize those features of the problem that are nonuniversal. That is, we require an equation of state which has nowhere near the same level of generality as the laws of thermodynamics themselves. Again, one turns to models whose aim is a characterization of the properties of matter. Different gases in different density regimes are appropriately described by different equations of state.

These examples, and others like them, allow us to discern three distinct levels of model building, though admittedly the boundary between them is blurred. In particular, the level of such modeling might be divided into (i) *fundamental laws*, (ii) *effective theories* and (iii) *constitutive models*. Our use of the term 'fundamental laws' is meant to include foundational notions such as Maxwell's equations and the laws of thermodynamics, laws thought to have validity independent of which system they are applied to. As will be seen in coming paragraphs, the notion of an 'effective theory' is more subtle, but is exemplified by ideas like elasticity theory and hydrodynamics. We have reserved 'constitutive model' as a term to refer to material-dependent models which capture some important features of observed material response.

To make the distinction between effective theories and constitutive models more clear, we consider both elastic and hydrodynamic theories in more detail. The existence of elasticity theories is an example of what we mean by an effective theory. The central thrust of such theories is that some subset (or linear combination or average) of the full microscopic set of degrees of freedom is identified as sufficing to characterize that system, or alternatively, the system is described in terms of some new phenomenological degrees of freedom (i.e. an order Indeed, one of the threads of recent scientific endeavor is the contention that reductionistic dogma is unfit to describe *emergent* properties in which it is the synthetic properties of the many-particle problem itself that yield many of the fascinating phenomena of current interest. Generally, we do not undertake a structural analysis of the Golden Gate Bridge or the beautiful convective patterns seen in the clouds from an airplane window on an atom by atom basis. These examples lead more naturally to effective descriptions in which one imagines the identification of an order parameter that characterizes the emergent property, and for which there is some appropriate continuum description.

Once the degrees of freedom have been identified, a dynamics of these degrees of freedom is constructed. To continue with our elaboration of the sense in which both elasticity and hydrodynamic theories serve as paradigmatic examples of such thinking, we note that in the case of elasticity (we have yet to say precisely which elastic *constitutive* model we have in mind) the characterization of the system is in terms of kinematic quantities such as displacements and strains which are themselves surrogates for the full atomic-level description of the system. Similarly, in the hydrodynamic context, velocities and strain rates replace an atom by atom description of the system. What all of these examples have in common is their reliance on a truncated description of material response in which the underlying discrete nature of the material is abandoned and is replaced by an effective theory in which microscopic processes have been subsumed into material parameters.

A key feature of the types of effective theories introduced above is that they depend upon the existence of a set of parameters that the theory itself is unable to determine. The elastic modulus tensor arises in describing linear elastic materials and the viscosity serves to characterize the hydrodynamic response of fluids. Similarly, the thermal conductivity arises in contemplating continuum models of heat conduction, while the magnetic susceptibility and the dielectric constant (to name a few) reflect a material's response to electromagnetic fields. What we learn from this observation is that normally effective theories like those described above must be tied to constitutive models which serve to distinguish one material from the next. Hence, we see that in addition to the level of modeling that is done in constructing the effective theory in the first place, there is a second key step in the modeling process in which *material specificity* is introduced. The elaboration of these various levels of modeling is one of the primary missions of the remainder of the book.

1.2.3 Case Studies in Modeling

One subbranch of materials science that has especially benefited from cross fertilization from different fields is that of the mechanical behavior of materials, itself one of the primary thrusts of the modeling efforts to be described in this book. The traditional disciplines of mechanical and civil engineering draw from the repository of information concerning the behavior of structural materials under both thermal and mechanical loading, with resulting structures from the Eiffel Tower to spacecraft that carry out 'fly-by' missions to distant planets. At more human size scales such as in the use of materials in applications ranging from lubricants on magnetic recording disks to the tungsten filaments that light millions of homes each evening, the interface between chemistry, materials science and condensed matter physics is obvious. Some of the issues that arise in the treatment of problems like these are the role of chemical impurities in either hardening materials or weakening grain boundaries, the ways in which microstructural size and shape influence both yield strength and ultimate resistance to fracture and the dazzling number of processing steps that attend the development of key technologies such as the Pentium chip which presides over the computer on which I am writing these words. Our discussion thus far has emphasized the mechanics of constructing models of material response without illustrating the outcome of using them. In the present section, our aim is to show in qualitative terms the different sorts of models that might be set forth for modeling materials and what is learned from them.

Modeling Phase Diagrams. Earlier we noted that phase diagrams form one of the main backbones of materials science and are a fertile setting within which to pose many of the most interesting questions about materials. Dirac argued that once the Schrödinger equation was in hand, the rest of chemistry was just a matter of implementing sufficiently powerful numerical schemes for solving the relevant governing equations. To be exact, he noted in 1929:

> The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation.

Indeed, Dirac could have extended the scope of his claim to many problems in the study of materials, including phase diagrams, as problems in which the underlying governing equations are known, but which are at the same time characterized by oppressive complexity. On the other hand, an alternative argument can be made in that much of the most interesting physics present in treating problems with a high level of complexity such as phase diagrams is exactly that which we learn from trying to *avoid* the brute force calculation hinted at in Dirac's assertion. In particular, the physics of effective theory construction is precisely the business of replacing the brute force solution of the governing equations with some simpler description. Indeed, to enliven the discussion with dueling quotes we note that P. W. Anderson (1972) has remarked on this hierarchy of theories as follows:

> But this hierarchy does not imply that science X is 'just applied Y'. At each stage entirely new laws, concepts, and generalizations are necessary, requiring inspiration and creativity to just as great a degree as in the previous one. Psychology is not applied biology, nor is biology applied chemistry.

To which we might add that modeling complex many degree of freedom systems is not just an application of what is already known about single degree of freedom systems. To my mind, one of the most exciting current activities in the physical sciences is precisely this self-conscious attempt to systematically eliminate degrees of freedom so as to construct theories demanding minimal information.

In chap. 6, we will take up the subject of phase diagrams, with special attention being given to the computation of such diagrams on the basis of atomic-level insights. One of the insights that will become evident when we delve into these questions more deeply is the large extent to which computing phase diagrams represents the confluence of ideas and methods from many distinct sources. On the one hand, these calculations demand the total energies of all of the imagined

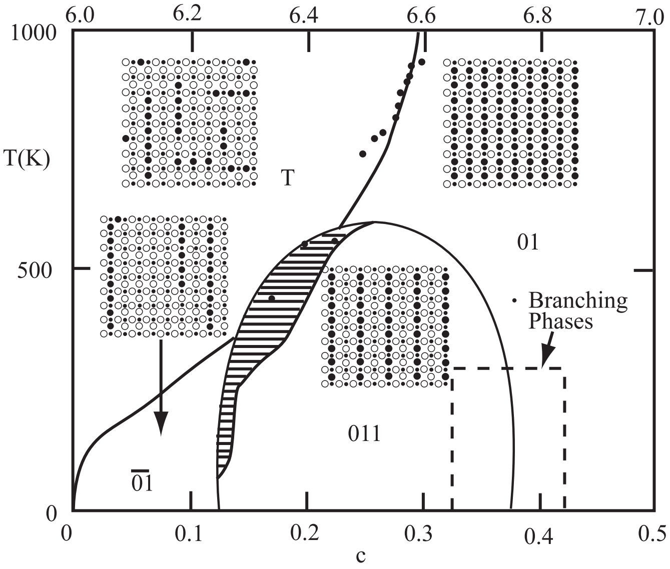

Fig. 1.7. Phase diagram for oxygen ordering in the YBCO class of high-temperature superconductors (after Ceder (1994)).

structural competitors which is the playing out of solving the Schrödinger equation referred to above. The calculation of such energies will be one of the centerpieces in the chapters to follow. In addition, once these energies are obtained, they must be supplemented by statistical arguments for assessing the entropy associated with both configurational disorder and the presence of thermal vibrations. It will be seen that in some instances it is possible to use an effective Ising representation of the various structural competitors to replace the laborious case by case search over different structural competitors.

An example of the computed and measured phase diagrams for oxygen ordering in the Cu–O high-temperature superconductors is given in fig. 1.7. The basic idea is the construction of an effective description of the energetics of the various structural competitors and to rank order these competitors as a function of some control parameters such as the composition and the temperature. For each point in parameter space, the victor in this competition is the equilibrium structure. We will come back later to some of the explicit details involved in computing the phase diagram of fig. 1.7 and note for the time being only that the calculation of such phase diagrams is a key part of computational materials science.

Modeling Material Parameters. In section 1.1.1, we argued that in many instances an extremely powerful idea is that of a material parameter. Whether discussing elasticity, heat conduction, mass transport or magnetism, we can capture the particulars of a given material in terms of such parameters. As already alluded to, the continuum models of heat conduction or mass transport cannot instruct us as to why the values of transport coefficients in some materials are large while in others they are small. Consequently, an important mission in the attempt to figure out what makes materials tick is the ambition of deducing material parameters on the basis of microscopic models.

As a first reflection on calculations of this type, fig. 1.8 shows examples of the correspondence between macroscopic material parameters and a subset of the associated microscopic calculations that might be used to determine them. One example of the use of microscopic calculations to inform higher-level models concerning material parameters is that of the diffusion constant. One of the challenges posed by data on diffusion is its strong variability in the presence of 'short-circuit' diffusion pathways such as surfaces, grain boundaries and dislocations. From a microscopic perspective, the essential idea is to examine the energetics of the diffusing particle as it passes the saddle point connecting two different wells in the energy landscape. In this case, a conjecture is made concerning the dominant reaction pathway in terms of a reaction coordinate which provides a measure of the extent to which the system has passed from one state to the next. The energy at the saddle point is used to determine the activation energy for diffusion. This activation energy, in conjunction with a model of the frequency with which the diffusing species attempts to cross the barrier leads to the diffusion constant itself. The key point made in fig. 1.8 is the idea that the atomic-level calculations can be used to inform our understanding of a higher-level material parameter.

A second example revealed in fig. 1.8(c) and (d) is that of the thermal conductivity. The left hand frame shows the phonon dispersion relation for Ge (a subject we will return to again in chap. 5) as computed using microscopic analysis. The right hand frame shows the measured thermal conductivity itself. Without entering into details, we note that on the basis of a knowledge of both the phonon dispersion relation and the anharmonic coupling between these phonons, it is possible to build up an analysis of the thermal conductivity, again revealing the strategy of using microscopic calculations to inform our understanding of higher-level continuum quantities. These case studies are meant to exemplify the logical connection between microscopic calculations and material parameters. Much of the business of coming chapters will surround the details of such calculations.

Modeling Dislocation Cores. In an earlier section, we belabored the critical coupling of structure and properties, and this is another arena within which modeling can produce valuable insights. One of our insights concerning the importance of structure was that of the role of lattice defects in governing many