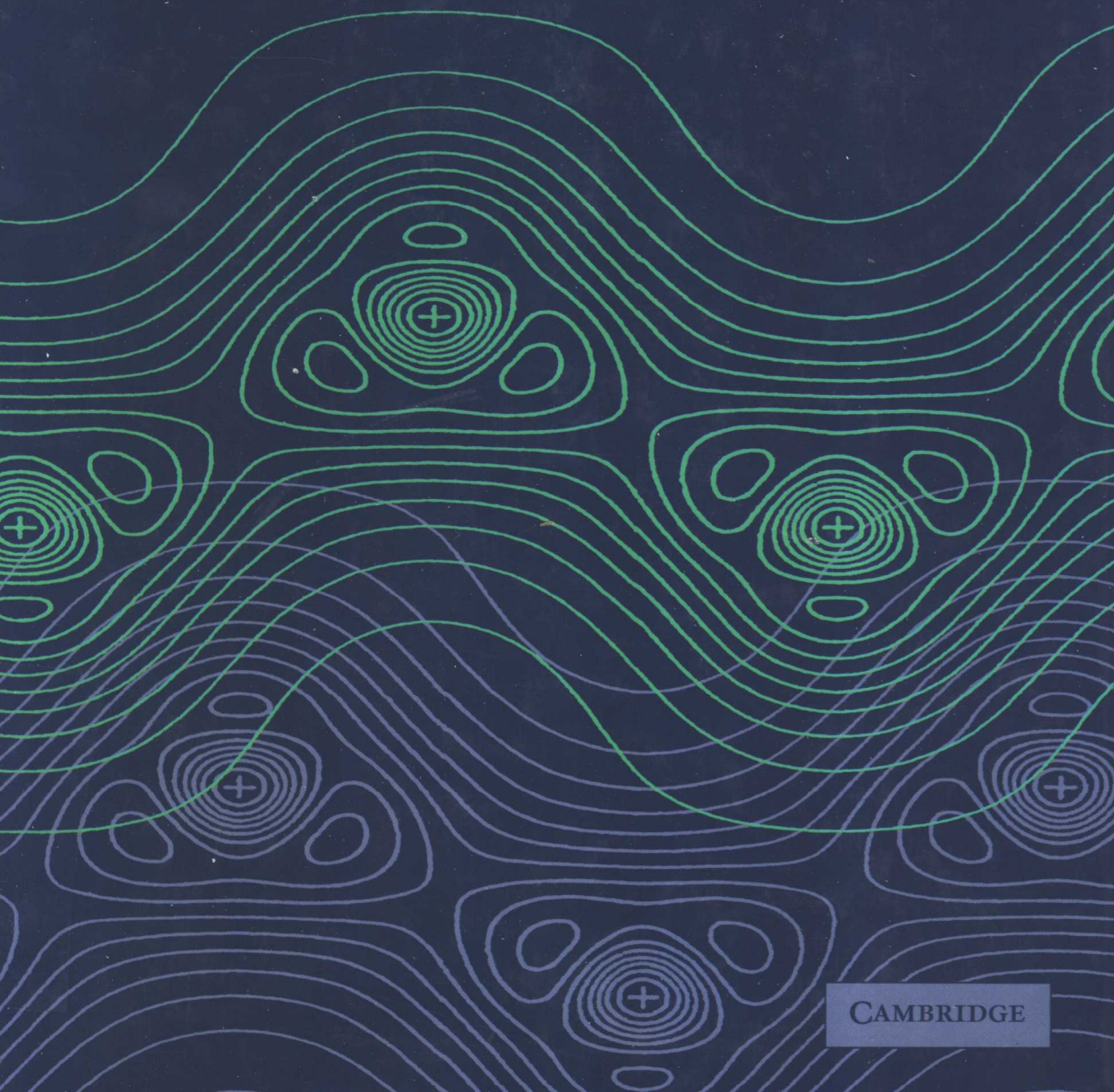


Electronic Basis of the Strength of Materials

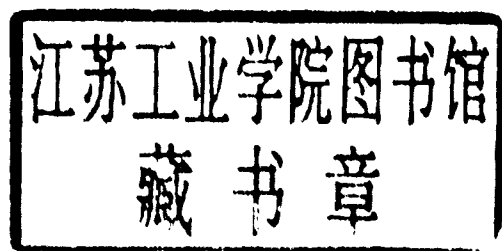
John Gilman



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ELECTRONIC BASIS OF THE
STRENGTH OF MATERIALS

JOHN J. GILMAN



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Preface

In the middle of the twentieth century it was recognized that the theory of the mechanics of continua (particularly solid mechanics) is not adequate to account for the strength properties of materials. It was clear that structural considerations at the microscopic and nanoscopic levels of aggregation are not only important but are essential to an understanding of the strengths of materials. It also came to be realized, as a result of the fact that plastic shear deformation is usually heterogeneous, that a space can be continuous but not simply connected, that is, dislocated. Also, in crystals, such dislocations are quantized, having constant displacements equal to the magnitudes of translation vectors of the crystal structure.

Although structural geometry plays an essential role in determining mechanical behavior, it leaves a number of questions unanswered. The answers to these questions can only be found by considering the electronic structure that underlies the geometric factors. Since the behavior of electrons is not described by classical mechanics, this necessitates the use of quantum mechanics to obtain answers to the various unanswered questions. For example, why is the shear stiffness of diamond greater than its volumetric stiffness? Why do the most simple metals, the alkalis, have body-centered cubic crystal structures which are not atomically close packed? Why is pure silicon brittle, while pure nickel is quite ductile? They both have the same crystal structure, so why is pure TiC hard, while pure NaCl is soft? Why do intermetallic compounds often change their color when they are plastically deformed? What determines the temperature dependences of yield stresses? Why are grain boundaries weak? What activates plastic flow and crack growth at low temperatures where there are no thermal fluctuations? Only the subatomic behavior of electrons can account for these phenomena. This is the theme of this book.

I recall seeing a review of a book (*Electronic Structure and the Properties of Solids*) by Walter Harrison that called it "idiosyncratic". It is that, but it is also comprehensive and instructive as only a lifetime of scholarship could make it. This book is also idiosyncratic. That is, it is one person's view of a vast and complex subject. Whether it is instructive is a verdict to be brought by readers.

This book differs from most books dealing with electronic structure which introduce the formalities of quantum mechanics, and then circumvent them with approximations and numerical computations. Here, it is assumed that solids are so complex that it is better to make the approximations first, and then try to show that they are consistent with the basic

rules of quantum mechanics, and that they yield properties consistent with the measured values. In this regard much use is made of Heisenberg's Theorem in its exact form, so there is nothing uncertain about it. It is an approximate solution of Schrödinger's equation.

Perhaps the most controversial topic in the book is that of dislocation mobility. Together with W.G. Johnston, the author made the first direct measurements of dislocation mobility, and therefore has some knowledge of its intricacies. The latter have not been described consistently in much of the extant literature. A purpose of this book is to correct this.

Sometimes explicitly, and often implicitly, the electronic properties on which the strength properties depend are the valence charge density, and the electronic polarizability. The reader should have a better appreciation of this after reading this book. Since these are also the electronic properties that primarily determine the optical and the chemical properties, this demonstrates the unity that exists among the various properties.

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Section I

Introduction

The central property of a solid is its strength. Upon this property several engineering disciplines have been built. First came the construction of shelter, and of ordnance for hunting and war, as well as tools for domestic use. Then came civil, mechanical, electrical, and chemical engineering; followed by electronics, aerospace, and now micro-device, optical, and biomedical engineering. Major civilizing events have resulted from advances in the strength of materials. The most dramatic was the industrial revolution which resulted directly from the jump in the strength of structures introduced by inexpensive steel. Before that, mining, weaving, military ordnance, agriculture, sailing, and various crafts advanced as material strengths increased. Inexpensive steel transformed the ways in which bridges, tunnels, and buildings were built and increased their sizes by orders of magnitude. It allowed fast, intricate, manufacturing machinery to be made such as that used for making textiles, for agriculture, for printing, and for manufacturing objects. The power levels of steam and gas engines were increased ten-thousand-fold when it became available. This revolutionized transportation on land through railways, and at sea through steam-powered ships. The unprecedented strength, ductility, and economy of steel affected every aspect of the way the world functioned. Unfortunately, it also led to increased destruction in war.

More recently society has been impacted in a major way by the inexpensive air travel that is a direct result of the remarkable strength of nickel–aluminum alloys at high temperatures. For the future, the high strength of pure silicon crystals is being exploited in micro-electronic devices, as well as the strength combined with the optical properties of oxides for optical and materials processing systems. So the importance of the strength of materials to the structure and activities of the world seems clear.

The essence of “solidity” is the ability of a solid to resist shearing forces that try to change its shape. Of all known materials, diamond possesses this ability in the highest degree, and therefore may be considered to be the most “solid” of all substances. In contrast, pure lead is very deficient in this ability. It is much more like a very viscous liquid than a true solid, and if pure, slowly creeps under its own weight. Why the difference? An answer can only be given in terms of the quantum mechanics governing atomic physics. No adequate answer is given by classical continuum mechanics.

The nature of the strength of solids is much more complex than it initially may appear to be. Strength cannot be characterized by a single measurement because, for example, the

failure of a filament in simple tension is quite different from the failure of a tubular shaft in torsion. Also, in compression, failure may occur by buckling, but this does not happen in tension. Thus “strength” is a group of properties, not a single one. If forces are applied to a solid object, there are various ways in which it may fail to support them. It may not have enough elastic stiffness. For example, helicopter rotor blades must be stiff enough elastically not to sag (deflect) more than a moderate amount. They must neither droop to the ground when the helicopter is stationary, nor bend upward in flight so much that they cease to generate adequate lift. One of the first challenges faced by the Wright brothers was how to keep the wings of their gliders from deflecting too much.

Although an object may have enough elastic stiffness, it may not have enough resistance to plastic flow. That is, its yield stress may be too low. For example, copper tubing is limited in the amount of water pressure it can sustain by its yield stress. Or, the blades of a high speed turbine may plastically flow slowly (creep), so the turbine fails prematurely. Successful aircraft turbines could not be built in the early part of the twentieth century because of this problem.

A material may be elastically stiff, and resistant to plastic flow, but still fallible if it has low resistance to crack propagation; that is, it is too brittle. Window glass is a classic example. Its chemical bonds are very strong combinations of silicon and oxygen, but cracks propagate through it easily, so its practical strength is rather low. At high temperatures, some metals are elastically stiff, and flow (creep) only slowly, but they rupture because small voids open up in them. They are said to suffer from low stress-rupture strength; or they are said to be “hot short”.

In broad terms, resistance to these three failure modes defines what is meant by strength, but there are several complications. One is that the geometric configuration of a material together with the pattern of forces that are applied to it affect how successful it is in avoiding the deformations leading to failure. Some standard configurations are: columns, arches, cables, beams, shafts, shells, and frames (trusses). Each of these has its own characteristics, and behaves differently in tension versus compression versus torsion.

Temperature, time, and chemical reactivity all have large effects on strength. Materials become less solid-like as the temperature rises, until they melt or decompose. Time periods of interest range from the geological ($\sim 10^{15}$ s) to electronic response times ($\sim 10^{-14}$ s), a spread of nearly 30 orders of magnitude! Chemical reactivity may stabilize strength by forming a protective coating, or destabilize it by accelerating crack growth.

Given the large behavioral domain associated with strength, it is not realistic to expect to be able to develop a comprehensive quantitative theory of the behavior in terms of its atomic constituents. At best, the principal ideas regarding the microscopic phenomena that underlie the macroscopic behavior can be described and compared with observations. The set of principal ideas is, in fact, surprisingly small, while the overall complexity is very large. As a result, it is usually easier to measure strength properties than to try to carry out the elaborate calculations that might predict them from physical relationships. However, understanding the physics and chemistry that underlie strength is very useful because it indicates where the limits of the strength properties lie, and it suggests steps that can be

taken to improve the practical properties up to their limits. It also indicates how strength properties are related to other physical properties.

The behavior of structural systems is complicated as a result of inescapable interactions between an elastic macroscopic structure (it applies tractions), the elastic response of a material, and the plastic response of the material (or set of materials). Since they are both linear, the first two can usually be combined into one linear response, but plasticity is inherently non-linear. This results in very few situations for which algebraic solutions can be found, and often makes numerical analysis difficult, as well as unreliable. An added difficulty is that there is no equation of state for plastic deformation. Therefore, details of the mechanical history of a material must be taken into account in projecting its future behavior.

A key part of the description of strength is to relate the two kinds of elastic strain (change of volume at constant shape, and change of shape at constant volume) to fundamental physical behavior, and to understand how and why the stiffnesses vary systematically with chemical composition, that is, with positions in the Periodic Table of the Elements, and with various combinations of the elements. The explanation begins with the theory of cohesion which is based on the structures of atoms and the theoretical behavior of electrons.

If solids were perfectly uniform in their structure it would be a relatively simple matter to define their resistance to shearing forces. A single functional relation between stress and strain could be defined for each solid that would depend only on the strength of its atomic bonds and its crystal structure. However, most solids are not perfectly uniform in structure, but contain a heterogeneous host of internal defects. Their strengths are so sensitive to the presence of these defects that the definition of strength acquires great complexity. This structure sensitivity plus the behavioral complexity of electrons in polyelectron atoms is why no comprehensive theory can be expected.

One defect to which all solids are vulnerable is the crack. By acting as a highly efficient lever, a crack allows relatively small applied forces to break the internal atomic bonds of a solid, and thereby reduce its dilatational and shear resistances to zero.

Crystalline solids are also very vulnerable to dislocations. These defects allow shearing to cause shape changes with great ease because they can move and multiply readily, particularly in metals. Other defects which must be considered are atomic vacancies and interstitials, foreign atoms, phonons, excitons, and electrical (color) centers.

An engineering property such as fatigue strength, yield strength, or fracture strength is determined not only by atomic bond strengths, but also by the many defects and their interactions. This makes the subject rich in detail, but often confusing, and sometimes treacherous for those seeking to develop it, or use it.

Time is a factor of primary importance in mechanical behavior. Indeed most of the distinction that is ordinarily made between liquids and solids is based on a shift of time scale. Slowly strained solids behave much like liquids, and liquids subjected to very high strain rates (above about 10^6 s^{-1}) behave much like solids.

In most cases, the resistance to plastic flow is determined by average dislocation mobilities, and these vary enormously (fluxes ranging from zero to approximately $10^{12}/\text{cm}^2$)

depending on the primary, secondary, and tertiary chemical structure of a material. Not only classical microstructural mechanics is involved, but also quantum-chemical mechanics. Indeed, if electrons were not limited in their behavior by the Pauli Principle of quantum mechanics, it would be a mushy world! It is the localization of electrons required by the Pauli Principle that leads to covalent bonds, and thence to the hard solids of which diamond is the prototype.

Understanding of strength properties in terms of microscopic mechanisms has been relatively slow to develop. In part this has resulted because these properties range so widely over a multitude of variables; and they depend in quite subtle ways on the underlying electronic structures of solids. The range of the properties is approximately the same as that of electrical conductivity for which the ratio of the maximum to the minimum is about 10^{32} . The analogous mechanical transport property is the plastic deformation rate. This has been observed as low as 10^{-16} s^{-1} and, under shock loading conditions, as high as 10^{14} s^{-1} , for a ratio of 10^{30} . Thus the range is similar to that of the electrical resistivity.

It has gradually become clear that detailed knowledge of the nature of the chemical bonding between the atoms of a solid is crucial to an adequate understanding of strength. Chemical bonding is provided by electronic structure. This depends, in turn, on the unique properties of electrons (namely, their charges, masses, wavelengths, phases, and spins).

The sizes of atoms are determined by energies of the electrons in their occupied quantum states. Atomic "shapes" also play a role. These are determined by the angular momenta of the electrons in the occupied energy states. Interactions between the atoms provide cohesion through a rearrangement of the distribution of the valence (bonding) electrons between pairs, and larger clusters of atoms. This electron distribution depends, in addition to other factors, on the "spins" of the electrons which are constrained by the Pauli Exclusion Principle. Therefore, the details of the spacial distributions of the bonding electrons determine the strength properties, not just the average electron energies.

There are four primary properties to be considered: cohesion, elastic stiffness, plastic yield stress, and ductility (fracture). Additionally, there are many secondary properties, but the four primary properties are the crucial ones in the construction of load-bearing structures, and the discussion here will be concerned with relating them to:

- (1) the properties of atomic particles (electrons, ion cores, photons, phonons, etc.),
- (2) the bonding of atoms (covalent, metallic, ionic, and dispersive),
- (3) extrinsic and intrinsic dislocation mobilities,
- (4) the behavior of cracks.

It will be assumed that the reader has some knowledge of macroscopic solid mechanics, and therefore with the standard terminology. It will also be assumed that the reader has been introduced to atomic physics, although the pertinent aspects of this will be reviewed. The mathematical level of the discussion will be that of undergraduate physics.

Section II

Elements of solid mechanics

1

Nature of elastic stiffness

The theory of elasticity is a structure of beauty and complexity. No one person sat down and wrote it out. From its first glimmerings in the mind of Galileo (ca. 1638) to the settlement of the question of the minimum number of coefficients required to specify a general elastic response took about 250 years. The latter work was done by Voigt (ca. 1888). Even then very little was known about the underlying factors that determine the coefficients; that is, the chemical properties that determine how resistant a material is to changes in its volume (the bulk modulus), and changes in its shape (the shear moduli). Even now the theory of shear moduli is only partially satisfactory.

Given the ongoing controversy regarding which comes first, practice or science, it is of interest to note that the early history of the theory of elasticity was motivated by the practical interests of those who made the important early advances. Leonardo da Vinci was interested in the design of arches. Galileo was concerned with naval architecture. Hooke wanted to make better clock springs. And Mariotte needed to build effective water piping to supply the palace at Versailles.

Complexity in the theory of elasticity is unavoidable because elastic behavior is intrinsically three-dimensional. Furthermore, most materials are not structurally isotropic; they have textures. Something as simple as a wooden post with a square cross-section looks different, in general, along each of the perpendiculars to its faces. These structural differences translate into different elastic stiffnesses in the three perpendicular directions. The situation is further complicated by the need to describe the shear responses in terms of a shear plane, plus a direction on the plane.

If forces are applied to the opposite ends of a slender bar, it will elongate or contract in proportion to the size of the forces (Hooke's Law). The coefficient of response is Young's modulus. However, the bar might also be twisted around its length, or it might be bent around an axis perpendicular to its length. The twisting mode of deformation requires another response coefficient, the shear modulus. If the slenderness of the bar is reduced to the limit of a line, both of its elastic moduli become meaningless. They cannot exist in the

absence of finite atoms, and the bonds between the atoms which are formed by electrons that behave according to quantum mechanics.

Consider a square mesh of wires soldered together at the intersections of the wires (a wire screen). Suppose a square piece is cut from the mesh with the edges of the square parallel to the wires. If forces are applied parallel to the edges of the square, the response will be stiff, whereas if forces are applied parallel to one of the diagonals of the square, the response will be relatively soft. Thus two distinctly different response coefficients are needed to describe the square's mechanical behavior.

Next imagine a three-dimensional framework of wires in a cubic array soldered together at the nodes of the wires (on a larger scale this would be like the framework of a steel building with all of the girders of the same length). This will have three different response coefficients in general: one for forces applied parallel to the wires, another for forces applied parallel to the diagonals of the faces of the cubes, and the third for forces applied along the diagonals of the cubes (lines connecting the opposite far corners). The three coefficients can be reduced to two by adjusting the design of the nodes; then the structure is said to be elastically isotropic.

More response coefficients will be required if the symmetry of the structure is less than that of a cube. For example, if the framework consists of rectangular parallelepipeds, the number of coefficients increases to nine (orthorhombic symmetry). Then if the number of different lengths is reduced from three to two (tetragonal symmetry), the number of coefficients drops from nine to six; and if the number of different lengths is further reduced to one, only three coefficients are needed (cubic symmetry) as already indicated.

Clearly, a standardized framework is necessary within which the elastic coefficients can be defined. This is provided by tensor calculus which, as the name suggests, was devised for this purpose. It is necessarily more complex than vector calculus because the elastic state of a solid requires both tensions (or compressions) and shears to describe it.

The first step is to define what is meant by *stress* and by *strain*. This will include a definition of the notation that is used to distinguish the various possible components of the stress and strain tensors. Then the response coefficients that connect them can be defined.

One of the purposes of this book is to show how the response coefficients (elastic constants) are determined by the chemical and physical constitutions of various solids. This involves the interior geometry of the solid, and its corresponding electronic structure.

Temperature and time both have small and large effects on elastic stiffness depending on the material. At very low temperatures elastic stiffness becomes independent of temperature, but at higher temperatures (near the Debye temperature and above) various *anelastic* effects occur. Then a given material has two stiffnesses: one for fast loading when there is too little time for anelastic relaxation (called the unrelaxed modulus), and the other for slow loading which allows relaxation to occur (called the relaxed modulus). The difference between these two stiffnesses is small for solids in which the atoms are densely packed. A much larger effect is found in less dense materials such as elastomers (rubber-like materials). In these, the molecules tend to curl up into coils which have high entropy because they can be formed in

many different ways. When applied tractions stretch them, there are fewer ways for them to coil so their entropies decrease. This increases their free energies, so they resist stretching, but relatively weakly. They are sometimes said to have “entropic elasticity”, as contrasted with the more usual “enthalpic elasticity”.

The elastic response coefficients are the most fundamental of all of the properties of solids, and the most important sub-set of them is the shear coefficients. If these were not sufficiently large, all matter would be liquid-like. There would be no aeronautical, civil, or mechanical engineering. Furthermore, modern micro-electronics, as well as opto-electronics would not be possible. The elastic stiffnesses set limits on how strong materials can be, how slowly geological processes occur, and how natural structures respond to wind and rain. This is why the scientific study that began with Galileo continues today.

Imagine a world in which everything has the same elastic stiffness. If all the bulk stiffnesses (the resistance to volume changes) were the same, nails could not be driven into wood, and plows could not turn earth. Or, suppose that the stiffness of aluminum were one-fifth as large as it actually is. Then the wing tips of large aircraft would drag on the ground because the elastic deflections would be so large. It is for reasons like these that the elastic properties of solids have great engineering significance, and why the theory of elasticity played such an important role in the histories of both engineering and physics.

The architecture of the theory of elasticity is now considered to be applied mathematics, but once was in the mainstream of the development of calculus and differential equations, as well as physics. For a long time (centuries), the elastic properties were coefficients to be measured and tabulated. Their relationship to the properties of atomic particles, and to one another, awaited the development of quantum mechanics. Although there remain some aspects of the theory that are not entirely satisfactory, the progress that has been made toward a general theory is impressive.

All forms of matter (gases, liquids, solids, plasmas, etc.) resist changes of volume, and the amount of this resistance is measured by means of the bulk modulus. Its inverse is the compressibility. Solids are defined by their shear stiffness moduli. These have inverses called shear compliances. Since the shear response is difficult to separate from the volumetric response, the overall description of elastic behavior is complicated.

The primary factor determining elastic stiffness is chemical constitution because it determines the internal bonding. Broadly, there are four kinds of bonding: covalent, ionic, metallic, and molecular. Each has its idiosyncrasies. The stiffest bonds are of covalent character, while the least stiff are molecular.

In addition to their shear stiffnesses, solids have another special feature. They can be either perfect, nearly perfect, or imperfect, in terms of their structural geometry. An ideal, or perfect, solid has a specific crystal structure, and each site of the crystal structure is occupied by a specific atomic species. However, virtually all solids contain defects, including thermal vibrations, vacancies, interstitials, impurity atoms, dislocations, stacking faults, domain boundaries, and grain boundaries. These affect the elastic stiffness, particularly the shear stiffness.

The time dependence of elasticity, or *anelastic* response, results from a variety of effects. Some of these are the thermo-elastic effect, the hopping of carbon atoms in iron (Snoek effect), and the stress-induced ordering of atomic pairs in some alloys. The anelasticity of elastomers (rubber) is a much larger effect.

Changes of shape (strains) can be induced by fields other than stresses. Electric fields cause electrostriction, or piezoelectric strains; and magnetic fields cause magnetostriction.

An aim here is to describe the connections of the various response coefficients to chemical constitution. This is unlike many books on strength which describe the field variables, leaving the elastic stiffnesses as coefficients to be measured and tabulated.