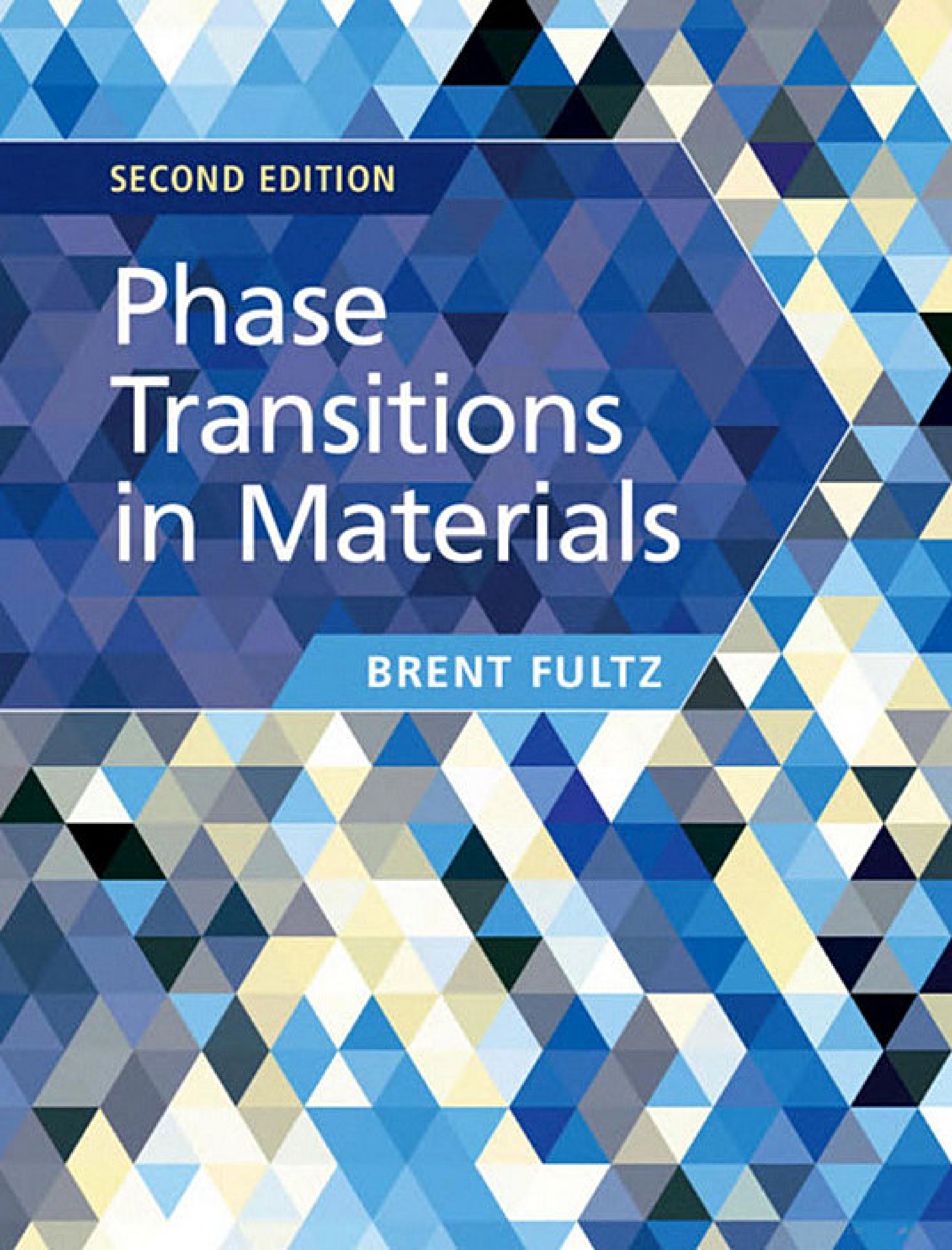

SECOND EDITION

Phase Transitions in Materials

BRENT FULTZ

Phase Transitions in Materials

Second Edition

The new edition of this popular textbook provides a fundamental approach to phase transformations and thermodynamics of materials. Explanations are emphasized at the level of atoms and electrons, and it comprehensively covers the classical topics from classical metallurgy to nanoscience and magnetic phase transitions. The book has three parts, covering the fundamentals of phase transformations, the origins of the Gibbs free energy, and the major phase transformations in materials science. A fourth part on advanced topics is available online. Much of the content from the first edition has been expanded, notably precipitation transformations in solids, heterogeneous nucleation, and energy, entropy, and pressure. Three new chapters have been added to cover interactions within microstructures, surfaces, and solidification. Containing over 170 end-of-chapter problems, it is a valuable companion to graduate students and researchers in materials science, engineering, and applied physics.

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Second Edition

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California Institute of Technology

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Preface

Content

This book explains the thermodynamics and kinetics of most of the important phase transitions in materials science. It is a textbook, so the emphasis is on explanations of phenomena rather than a scholarly assessment of their origins. The goal is explanations that are concise, clear, and reasonably complete. The level and detail are appropriate for upper division undergraduate students and graduate students in materials science and materials physics. The book should also be useful for researchers who are not specialists in these fields. The book is organized for approximately sequential coverage in a graduate-level course. The four parts of the book serve different purposes, however, and should be approached differently.

Part I presents topics that all graduate students in materials science must know.[1] After a general overview of phase transitions, temperature–composition phase diagrams are explained from classical thermodynamics and from the statistical mechanics of Ising lattices. Diffusion, equilibration, and nucleation are then covered, and general aspects of diffusion and nucleation are used with T–c phase diagrams to explain the rates of some phase transformations.

Part II addresses the origins of materials thermodynamics and kinetics at the level of atoms and electrons. Electronic and elastic energy are covered at the level needed in some of the later chapters. The physical origins of entropy (a topic that receives scant coverage in other texts) are presented in the context of phase transitions on Ising lattices. Effects of pressure, combined with temperature, are explained with a few concepts of chemical bonding and antibonding. The thermodynamics of real materials typically involves minimizing a free energy with multiple degrees of freedom, and Chapter 9 shows directions beyond one variable. Chapter 10 on kinetics emphasizes atom movements for diffusion in solids, especially features of atom–vacancy interchanges.

Part III is the longest. It describes important phase transformations in materials, with their underlying concepts. Topics include surface phenomena, melting, solidification, nucleation and growth in solids, spinodal decomposition, phase field theory, continuous ordering, martensitic transformations, phenomena in nanomaterials, and phase transitions involving electrons or spins. Many topics from metallurgy and ceramic engineering are

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[1] The author asks graduate students to explain some of the key concepts at a blackboard during their Ph.D. candidacy examinations.

covered, although the connection between processing and properties is less emphasized, allowing for a more concise presentation than in traditional texts.

The online Advanced Topics present modern topics that have proved their importance. These chapters are available online at doi:10.7907/05BY-QX43 and can be downloaded at no cost from https://www.library.caltech.edu. The chapters cover low- and high-temperature treatments of the partition function, nonequilibrium states in crystalline alloys, a *k*-space formulation of elastic energy, fluctuations and how they are measured, high-temperature thermodynamics, the renormalization group, scaling theory, and an introduction to quantum phase transitions. The topics are explained at a fundamental level, but unlike Parts I through III, for conciseness there are more omissions of methods and steps.

Many topics in phase transitions and related phenomena are not covered in this text. These include: polymer flow and dynamics including reptation, phase transitions in fluid systems including phenomena near the critical temperature, crystallographic symmetry in displacive transformations, and massive transformations. Also beyond the scope of the book are computational methods that are increasingly important for studies of phase transformations in materials, including: Monte Carlo methods, molecular dynamics methods (classical and quantum), and density functional theory with time or ensemble averages for materials at finite temperatures.

The field of phase transitions is huge, and continues to grow. This text is a snapshot of the field taken from the viewpoint of the author near the year 2020. Impressively, this field continues to offer a rich source of new ideas and results for both fundamental and applied research, and parts of it will look different in a decade or so. I expect, however, that the core will remain the same – the free energy of materials will be at the center, surrounded by issues of kinetics.

Teaching

I use this text in a course for Ph.D. students in both materials science and in applied physics at the California Institute of Technology. The 10-week course is offered in the third academic quarter as part of a one-year sequence. The first two quarters in this sequence cover thermodynamics and statistical mechanics, so the students are already familiar with using a partition function to obtain thermodynamic quantities. Familiarity with some concepts from solid-state physics and chemistry is certainly helpful, but the text develops many of the important concepts as needed.

In the one-quarter course at Caltech, I cover most topics in Parts I and II, moving in sequence through the chapters. Time limitations force a selection of topics from Part III and Advanced Topics. For example, I tend to cover Chapters 12, 16, 18, and parts of 14, 19, 20 (although sometimes these later parts are replaced by an advanced chapter, such as 25). It is unrealistic to cover the entire content of the book in one course, even with a 15-week semester. An instructor will use discretion in selecting topics for the second half of his or her course.

The problems at the end of each chapter were used for weekly student assignments, and this helped to refine their wording and content. The majority of these problems are based on concepts explained in the text, sometimes filling in explanations or extending the analyses. Other problems, less popular with students, develop new concepts not described in the chapter. These problems usually include longer explanations and hints that may be worth reading even without working the problem. None of the problems are intended to be particularly difficult, and some can be answered quickly with one main idea. For homework, I assign five or six of these problems every week during the term. In their reviews of the course, most students reportedly spend 6–8 hours per week outside the classroom completing these problem sets and reading the text. An online solutions manual is available to course instructors whose identity can be verified. Please ask me for further information.

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I thank J.J. Hoyt for collaborating with me on a book chapter about phase equilibria and phase transformations that prompted me to get started on the first edition of this book. The development of the topic of vibrational entropy would not have been possible without the contributions of my junior collaborators at Caltech, especially L. Anthony, L.J. Nagel, H.N. Frase, M.E. Manley, J.Y.Y. Lin, T.L. Swan-Wood, A.B. Papandrew, O. Delaire, M.S. Lucas, M.G. Kresch, M.L. Winterrose, J. Purewal, C.W. Li, T. Lan, H.L. Smith, L. Mauger, S.J. Tracy, D.S. Kim, and N. Weadock. Several of them are taking this field into new directions.

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Brent Fultz

Notation

a	lattice parameter
A	area
$\vec{A}$	vector potential of magnetic field
A-atom	generic chemical element
APDB	antiphase domain boundary
α	coefficient of linear thermal expansion
α	critical exponent for heat capacity
α-phase	generic phase
α-sublattice	a lattice of like atoms within an ordered structure
α_i	root of Bessel function
α^2	electron–phonon coupling factor
$\vec{b}$	Burgers vector of dislocation
b_{A}	coherent neutron scattering length of isotope A
$b(\vec{k})$	Fourier transform of pairwise energy for two concentration waves
B	bulk modulus
$\vec{B}$	magnetic field
B-atom	generic chemical element
$B(\vec{R})$	pairwise energy between atoms
β	coefficient of volume thermal expansion
β	critical exponent for density
β-phase	generic phase
β-sublattice	a lattice of like atoms within an ordered structure
c	chemical composition (atomic fraction)
c_{l}^*	chemical composition of liquid at liquid–solid interface
c_{s}^*	chemical composition of solid at liquid–solid interface
c	speed of sound or light
c_{A}	concentration of A-atoms
c_{A}	weight of atomic wavefunction on atom A in a molecular wavefunction
C_{el}	electronic heat capacity
$C_P(T)$	heat capacity at constant pressure
$C_V(T)$	heat capacity at constant volume
C_{ij}, C_{ijlm}	elastic constant

D	diffusion coefficient
D	deformation potential
D_h	thermal (heat) diffusion coefficient
$\vec{D}$	electric polarization
D_0	prefactor for exponential form of diffusion coefficient
$\tilde{D}(c)$	interdiffusion coefficient
$\underline{D}(\vec{k})$, $D_{ij}(\vec{k})$	dynamical matrix, element of
δ	fractional change in volume (of misfitting sphere)
ΔG_V	change in Gibbs free energy per unit volume
ΔG^*	activation barrier for nucleation
$\Delta(\vec{r})$	static wave of chemical concentration

e	charge of electron
e_A	energy of an A-atom on a crystal site
e_AB	energy of a pair (bond) between an A- and a B-atom
e_R, e_W	energy of two atoms, A and B, on their right or wrong sublattices
$\vec{e}_{\kappa j}(\vec{k})$	polarization for atom of basis index κ in phonon of $\vec{k}$ in branch j
$\mathrm{erf}(z)$	error function
E	energy, thermodynamic energy
$\vec{E}$	electric field
E_el	elastic energy
E_elec	electrostatic energy
ε	energy, energy of phonon
ϵ	energy, energy of electron
ϵ	fractional difference in T from T_c
ϵ_F	Fermi energy
ϵ_j, ϵ_{ij}	strain
η	fractional change of lattice parameter with composition
η	order parameter

f	correlation factor
f_α	(atomic) fraction of α-phase
f_j	interaction free energy
$f(c)$	free energy per unit volume
F	Helmholtz free energy
$\mathcal{F}$	force
$F_\xi(c, T)$	free energy for phase ξ with composition c at temperature T

$g(\varepsilon)$	phonon density of states
$\vec{g}$	reciprocal lattice vector
$\mathbf{grad}(c)$ or $\overrightarrow{\nabla c}$	gradient (of concentration)
G	Gibbs free energy
$G(\vec{r}, t)$	Van Hove space-time correlation function

$\mathcal{G}$	temperature gradient $\mathrm{d}T/\mathrm{d}x$
γ	coefficient for linear electronic heat capacity vs. T
γ	Grüneisen parameter
γ_j	Grüneisen parameter for phonon mode j
γ_{xy}	shear strain
Γ	atomic jump frequency
Γ	point at origin of reciprocal lattice
h	bond integral
$\hbar$	Planck constant divided by 2π
H	Hamiltonian
$\vec{H}$	magnetic field
$\vec{j}$	flux
$J_0(x)$, $J_1(x)$	Bessel functions of zero and first order
J_n	number of clusters per unit time that change from n to $n+1$
J_{ss}	steady-state flux in number space of cluster sizes
J_{hs}, J_{hl}	heat flux in solid and liquid (1D)
$\vec{J}_{\mathrm{A}}$	flux of A-atoms
$J(\vec{r}_1 - \vec{r}_j)$	magnetic exchange energy
k	partitioning ratio $k = c_{\mathrm{s}}/c_{\mathrm{l}}$
$\vec{k}$	wavevector
k_{B}	Boltzmann constant
κ	coefficient for square gradient energy
κ	Ginzburg–Landau parameter
L	latent heat
L	long-range order parameter
$L(\tau E_0/k_{\mathrm{B}}T)$	Langevin function
LHS	left-hand side
λ	wavelength
λ	electron–phonon coupling parameter
m	mass
m	slope of liquidus curve on phase diagram $\mathrm{d}T_{\mathrm{l}}/\mathrm{d}c$
M	mobility
$\vec{M}$	magnetization
$\mathcal{M}$	Mendeleev number
μ	chemical potential
μ	shear modulus
$\vec{\mu}$	magnetic moment

$n(\varepsilon_i, T)$	Planck distribution
N	number (of atoms)
N_{A}^{α}	number of A-atoms on α-sublattice (point variable)
$N_{\mathrm{AB}}^{\alpha\beta}$	number of A–B pairs with A on α and B on β (pair variable)
$N(k)$	number of quantum states with wavevector less than k
$\underset{\sim}{N}(t)$	vector of number occupancies of states at time t
ν	frequency
ν	Poisson ratio
ν	critical exponent for correlation length

ω	angular frequency
Ω	number of states accessible to the system
Ω	atomic volume
Ω_j	configurations of a system with energy j

p_i	probability of a state
$\vec{p}$	momentum
p_{A}	partial pressure of vapor of element A
p_{A}^{α}	probability of A-atom on α-sublattice (point variable)
$p_{\mathrm{AB}}^{\alpha\beta}$	probability of A–B pair with A on α and B on β (pair variable)
P	pressure
P_{th}	thermal pressure (from expansion against a bulk modulus)
$\mathcal{P}$	Péclet number
$\Phi(r)$	interatomic, central-force potential
$\Phi_{\mathrm{M}}(r)$, $\Phi_{\mathrm{L\text{-}J}}(r)$	Morse potential, Lennard-Jones potential
Φ_0	quantum of magnetic flux $hc/2e$

Q	compositional wavevector $2\pi/\lambda$
Q	total electrostatic charge
$\vec{Q}$	momentum transfer in scattering
$\boldsymbol{Q}$	quality factor of damped harmonic oscillator

r_{B}	Bohr radius $r_{\mathrm{B}} = \hbar^2/(m_e e^2)$
r_{WS}	Wigner–Seitz radius
$\vec{r}_l$	position of unit cell
$\vec{r}_k$	basis vector within unit cell
R	number of right atoms on a sublattice of an ordered structure
$R(Q)$	growth rate for compositional wavevector Q
R^*	critical radius for nucleation
$\vec{R}$	position of atom center
$\vec{R}_n$	displacement after n jumps
$\mathcal{R}$	number of atoms in unit cell
RHS	right-hand side

ρ	density, e.g., [atoms cm^{-3}]
$\rho(\epsilon)$	electronic density of states
$\rho(\epsilon_{\text{F}})$	electronic density of states at the Fermi energy

$\vec{s}_i$	electronic spin at site i
S	entropy
S	overlap integral
S_{conf}	configurational entropy
S_{vib}	vibrational entropy
S_{h}	harmonic entropy
S_{qh}	entropy contribution from quasiharmonicity
S_{anh}	entropy contribution from anharmonicity
S_{el}	electronic entropy
S_{epi}	entropy contribution from electron–phonon interaction
S_{mag}	magnetic entropy
$S(\vec{Q}, \omega)$	scattering function
σ	surface energy per unit area
σ	electrical conductivity
σ	spin number (± 1)
σ_{gb}	energy per unit area of grain boundary
σ_{ij}	stress

t	time
T	temperature
T_{c}	critical temperature
T_{C}	Curie temperature
T_{m}	melting temperature
T_{N}	Néel temperature
$T_1, T_2, \ldots$	sequence of temperatures such that $T_2 > T_1$
$\vec{T}$	translation vector of real space lattice
τ	characteristic time (e.g., for diffusion)
$\vec{\tau}$	electrostatic dipole moment

$\theta(\vec{r})$	Heaviside function, 1 in the region, 0 outside
$\theta(\vec{r}, t)$	phase of wavefunction in space and time
Θ_{D}	Debye temperature

$\vec{u}(x, y, z)$	displacement vector
U	difference in chemical preferences of A- and B-atoms $U = (e_{\text{AA}} - e_{\text{BB}})/4V$
U	Coulomb energy penalty for placing a second electron on a site in Hubbard model
Υ_j	Grüneisen parameter for energy of electronic state j

$\vec{v}$	velocity
V	interchange energy $V = (e_{\mathrm{AA}} + e_{\mathrm{BB}} - 2e_{\mathrm{AB}})/4$
V	volume
$V(\vec{r})$	potential energy
V_{Q}	quantum volume, related to cube of de Broglie wavelength
v_0	volume per atom
W	number of wrong atoms on a sublattice of an ordered structure
W_{ij}	transition rate from state j to state i
$W^{\uparrow}_{\beta\mathrm{A}\alpha}$	rate of increase of LRO parameter by jump of A from β- to α-sublattice
$\underset{\approx}{W}(\Delta t)$	transition matrix for time interval Δt
ξ	correlation function
ξ	length
$\{\chi_i\}$	reaction coordinates
χ	susceptibility
Y	Young's modulus
$\psi(\vec{r})$	wavefunction
z	coordination number of lattice
z	partition function of subsystem
Z	partition function
$\mathcal{Z}$	Zeldovich factor

PART I

BASIC THERMODYNAMICS AND KINETICS OF PHASE TRANSFORMATIONS

The field of phase transitions is rich and vast, and continues to grow. This text covers parts of the field relevant to materials physics, but many concepts and tools of phase transitions in materials are used elsewhere in the larger field of phase transitions. Likewise, new methods from the larger field are now being applied to studies of materials.

Part I of the book covers essential topics of free energy, phase diagrams, diffusion, nucleation, and a few classic phase transformations that have been part of the historical core of materials science. In essence, the topics in Part I are the thermodynamics of how atoms prefer to be arranged when brought together at various temperatures, and how the processes of atom movements control the rates and even the structures that are formed during phase transformations. The topics in Part I are largely traditional ones, but formulating the development in terms of statistical mechanics allows more rigor for some topics, and makes it easier to incorporate some deeper concepts from Part II into descriptions of phase transitions in Part III and the online Advanced Topics.

1 Introduction

1.1 What Is a Phase Transition?

A phase transition is an abrupt change in a system that occurs over a small range of a control variable. For thermodynamic phase transitions, typical control variables are the "intensive variables" of temperature, pressure, or magnetic field. Thermodynamic phase transitions in materials and condensed matter, the subject of this book, occur when there is a singularity in the free energy function of the material, or in one of the derivatives of the free energy function.[1] Accompanying a phase transition are changes in some physical properties and structure of the material, and changes in properties or structure are the usual way that a phase transition is discovered. There is a very broad range of systems that can exhibit phase transitions, including atomic nuclei, traffic flow, and social networks. For many systems it is a challenge to find reliable models of the free energy, however, so thermodynamic analyses are not available.

Interacting Components

Our focus is on thermodynamic phase transitions in assemblages of many atoms. How and why do these groups of atoms undergo changes in their structures with temperature and pressure? It is often useful to consider separately the components of the atoms:

- nuclei, which have charges that define the chemical elements,
- nuclear spins and their orientations,
- electrons that occupy states around the nuclei, and
- electron spins, which may have preferred orientations with respect to other spins.

Sometimes a phase transition involves only one of these components. For example, at low temperatures (microkelvin), the weak energy of interaction between spins at different nuclei can lead to a widespread alignment of nuclear spins. An ordered array of aligned nuclear spins may be favored thermodynamically at extremely low temperatures, but thermodynamics favors a disordered nuclear magnetic structure at modest temperatures. Order–disorder phase transitions have spawned several creative methods to understand how an order parameter, energy, and entropy depend on temperature.

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[1] A brief review of free energy is given in Section 1.6.2.

Sometimes phase transitions involve multiple physical components. Electrons of opposite spin can be coupled together by a wave of nuclear vibration (a phonon). These Cooper pairs can condense into a superconducting state at low temperatures. Perhaps electron charge or spin fluctuations couple the electrons in high-temperature superconductors, although the mechanism is not fully understood today. Much of the fascination with phase transitions such as superconductivity is with the insight they give into the interactions between the electrons and phonons, for example. While these are important subjects for study, they are to some extent diversions from the main topic of phase transitions. Likewise, delving deeper into the first example of nuclear spin alignments at low temperatures reveals that the information about the alignment of one nucleus is carried to a nearby nucleus by the conduction electrons, and these hyperfine interactions between nuclei and electrons are an interesting topic in their own right.[2]

Emergence of Macroscopic Behavior from the Atomistic

In a study of phase transitions, it is easy to lose track of the forest if we focus on the interesting trees. Throughout much of this text, the detailed interactions between the components of matter are replaced with simplifying assumptions that allow for straightforward analysis. Sometimes the essence of the phase transition is captured well with such a simple model. Other times the discrepancies prove interesting in themselves. Perhaps surprisingly, the same mathematical model reappears in explanations of phase transitions involving very different aspects of materials. The ordering of nuclear spins has a natural parallel with the ordering of electron spins in a ferromagnetic material, although the origin of the magnetic moments, their coupling, and the temperature of ordering are completely different. More surprisingly, there is a clear parallel between these spin-ordering problems and chemical ordering in an alloy, where a random distribution of two chemical elements on a crystal lattice evolves into a pattern such as a chessboard with decreasing temperature.

A phase transition is an "emergent phenomenon," meaning that its large-scale features emerge from interactions between numerous individual components. Philosophers classify a phase transition as a type of "weak emergence" because the large-scale properties can be predicted from the interactions of the individual components.[3] How emergence occurs is a topic in itself. When a change in temperature or pressure favors a new phase, it can appear abruptly with macroscopic dimensions, or it can grow continuously from the atomic scale to the macroscopic. Although the atomic-scale processes are statistical, the averaged macroscopic behavior is quite consistent for the same material under the same conditions.

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[2] At familiar temperatures the nuclear spins are completely disordered, and do not change in a way that affects the thermodynamics of the material. On the other hand, we might expect a coupling between chemical order and magnetic order if the energy scales of their internal interactions are comparable.

[3] "Strong emergence," which cannot be predicted this way, may underlie the origin of consciousness or the soul.

The macroscopic behavior is usually predicted by assuming a material of infinite size, since Avogadro's number can often be approximated adequately as infinity.

1.2 Atoms and Materials

An interaction between atoms is a precondition for a phase transition in a material (and, in fact, for having a material in the first place). Atoms interact in interesting ways when they are brought together. In condensed matter there are liquids of varying density, and numerous types of crystal structures. Magnetic moments form structures of their own, and the electron density can have spatial patterns. In general, chemical bonds are formed when atoms are brought together. The energy of interatomic interactions is dominated by the energy of the electrons, which are usually assumed to adapt instantaneously to the positions of the nuclei. The nuclei, in turn, tend to position themselves to allow the lowest energy of the material, which means that nuclei move around to let the electrons find low-energy states. Once the electronic structure of a material is known, it is often possible to understand many properties of a material, especially its chemical, electronic, magnetic, and optical properties.

For many materials, accurate calculations of electronic structure have arrived. Many reliable quantum mechanical calculations are now routine, and more will be commonplace soon. Electronic structure calculations are an important but large topic that extends beyond the scope of this text. Some aspects of electronic energy are explained in Chapter 6, and other aspects are developed as needed to explain specific phase transformations in Part III. (Fortunately, there are many excellent references on electronic energy and chemical bonding of materials.) Entropy is the other thermodynamic function essential for understanding most phase transitions in materials. Both the energy and entropy of materials

Box 1.1 **Microstructure**

Materials are made of atoms, but the structural arrangements of atoms are usually described by a hierarchy of features, each with its own characteristics. Mixtures of crystals and phases, with interfaces between them and defects inside them, are the "microstructure" of a material. One viewpoint is that a complete description of the structural features of microstructure is a full definition of the material. A second viewpoint adds excitations involving electrons, nuclei, or microstructure to the description of a material. The first viewpoint considers only matter, the second viewpoint adds energy to the definition of a material.

Control of microstructure is the means for controlling properties of a material – this is the central paradigm of materials science and engineering (see Fig. 1.1). Designing a microstructure is distinctly different from "Edisonian testing," which is another way to find materials with appropriate properties. Edisonian testing ignores the essence of a material, however, and is not materials science.

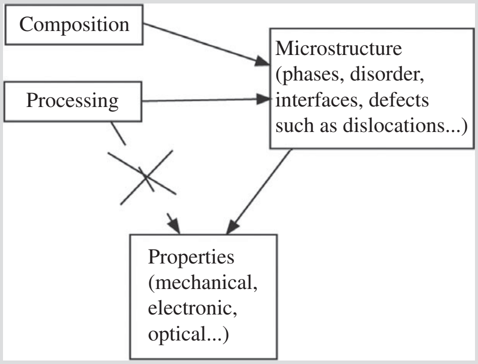

Figure.1.1 Paradigm of materials science. A direct processing-to-properties relationship, as Edison pursued when finding filament materials for incandescent light bulbs, is not materials science.

depend on the types of atoms and their mutual arrangements, parameterized as “state variables.” Careful selections of state variables are critical for developing predictive theories of phase transitions.

There are opportunities to control the states of matter through both thermodynamics and kinetics. Thermodynamic control tends to be the most reliable, at least when the atom motions are fast enough so that equilibrium can be approached in a reasonable time. Thermodynamic control involves selecting the chemical composition, and adjusting the intrinsic variables of temperature, pressure, and external fields. Control of temperature is usually the most accessible way to set the state of equilibrium, and has served us well through the bronze, iron, and silicon ages of humankind. Most of this book is concerned with phase transitions that are driven by temperature.

1.3 Pure Elements

1.3.1 Melting: A Discontinuous Phase Transition

A liquid and a crystal are fundamentally different owing to the symmetry of their atom arrangements. In Chapter 18 when the Landau–Lifshitz criterion for second-order phase transitions is developed, it is proved that melting must involve a discontinuity in the first derivative of the free energy, $\mathrm{d}F/\mathrm{d}T$, at the melting temperature. For now, please accept that it is not appropriate to use the same free energy function

$$F(T) = E - TS \tag{1.1}$$

for both the liquid and the solid phases. Instead, Fig. 1.2 shows two separate curves, $F_\mathrm{s}(T)$ and $F_\mathrm{l}(T)$, for the solid and liquid phases of a pure element. The curve $F_\mathrm{s}(T)$ for the solid lies below that of the liquid at $T = 0$ because the energy of the solid is lower than that of

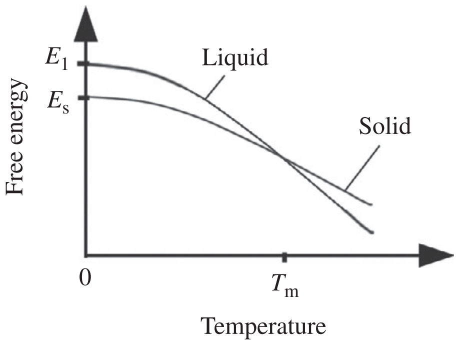

Figure 1.2 Free energy curves of a pure element when its atoms are arranged as a crystalline solid, $F_s(T)$, or as a liquid, $F_l(T)$.

the liquid.[4] As shown on the y-axis, $E_s < E_l$, and at $T = 0$ there is no entropy contribution to the free energy. The free energy of the liquid decreases faster with temperature than that of the solid because $S_s < S_l$.[5] The two curves $F_s(T)$ and $F_l(T)$ cross at the melting temperature, T_m.

In equilibrium, an elemental material follows the solid curve of Fig. 1.2 at low temperatures, and switches to the liquid curve above T_m. At T_m there is a discontinuity in the first derivative of the free energy. A "first-order" phase transition occurs. This is rather catastrophic behavior, with the material changing from all liquid to all solid over an infinitesimal range of temperature across T_m.

Pure elements have well-defined melting temperatures that are set by the equality of the solid and liquid free energies, $F_s(T_m) = F_l(T_m)$. For constant E and S, a consequence is obtained quickly

$$F_s(T_m) = F_l(T_m), \tag{1.2}$$

$$E_s - T_m S_s = E_l - T_m S_l, \tag{1.3}$$

$$S_l - S_s = \frac{E_l - E_s}{T_m} = \frac{L}{T_m}, \tag{1.4}$$

where the latent heat, L, a positive quantity, is defined with the difference in entropy at T_m

$$L \equiv \left[S_l(T_m) - S_s(T_m)\right] T_m. \tag{1.5}$$

The latent heat is absorbed at T_m during melting, and released during solidification.

Equation 1.4 for melting ignores the temperature dependences of E and S, which are important over a range of T. Nevertheless, if E and S in the solid and liquid vary slowly around T_m,[6] the two curves in Fig. 1.2 can be approximated as straight lines. At

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[4] Perhaps this is intuitive – the atoms in a crystalline solid have optimized their positions with respect to their neighbors, and all atoms are in such optimal positions. The liquid has bond distances and angles that are not at all uniform, meaning that some atoms are in configurations that are less favorable energetically.

[5] Again, perhaps this is intuitive – there are more equivalent ways Ω of arranging the atoms in the liquid than in a crystalline solid, so the entropy, $S = k_B \ln \Omega$, is larger for the liquid.

[6] It is actually the differences, $S_l - S_s$ and $E_l - E_s$, that should vary slowly with T, and this is more plausible.

temperatures very close to T_m, the difference in free energy of the liquid and solid is proportional to the undercooling

$$F_\mathrm{l}(T) - F_\mathrm{s}(T) = \frac{L\,(T_\mathrm{m} - T)}{T_\mathrm{m}} = \frac{L\Delta T}{T_\mathrm{m}}, \tag{1.6}$$

with the undercooling defined as $\Delta T \equiv T_\mathrm{m} - T$ (see Problem 1.3). The sign is correct in Eq. 1.6 – when $T < T_\mathrm{m}$, the $F_\mathrm{s}(T)$ is more negative (favorable) than $F_\mathrm{l}(T)$.

The thermodynamics of melting (or solidification) illustrates some general truths:

- The low-energy phase is favored at low temperatures.
- The high-entropy phase is favored at high temperatures.
- If the low-energy phase has a lower entropy than the other phase, there will be a phase transition at a finite temperature.

We now take a short digression into kinetics. Although a liquid will eventually solidify at any temperature below T_m, the rate of solidification depends strongly on ΔT. Equation 1.6 is useful for understanding the kinetics of solidification because it relates the undercooling below T_m to the difference in free energy of the liquid and solid. This difference in free energy is available to do work, such as overcoming any potential energy barriers that impede solidification. A larger undercooling makes it more probable for a small region of the liquid to overcome a nucleation barrier and become a solid,[7] and solidification speeds up considerably with undercooling. Equation 1.6 is based on thermodynamics, however. Kinetics requires additional information about the phase transformation. For example, Eq. 1.6 shows that the thermodynamics is symmetrical around T_m for solidification and melting (i.e., $F_\mathrm{l} - F_\mathrm{s} \propto \Delta T$ for both positive and negative ΔT), but the kinetics is not symmetrical. The enhanced kinetics of solidification with undercooling does not correspond to a more rapid melting with superheating. Melting does not have such a nucleation barrier.

1.3.2 Structural Symmetry and Continuous Phase Transitions

When the high-temperature phase and low-temperature phase have crystal structures with compatible symmetries, the phase transition can be continuous. Figure 1.3 is a map of the phases of cerium metal, charted in a space spanned by T and P, known as a "T–P phase diagram." Upon heating cerium at ambient pressure (0.0001 GPa), it transforms between four different crystalline phases before melting. Our present interest is in the phase transition between two of them, the α- and γ-phases.[8] Curiously, both have the fcc crystal structure, but they differ in volume by about 17% at ambient pressure. Choose a pressure of 1 GPa (to avoid the β-phase), and follow a vertical path in Fig. 1.3b that starts at low temperature, with cerium in the α-phase. Upon heating to a temperature near room

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[7] Chapter 4 discusses how the nucleation barrier originates from unfavorable surface energy and the large surface-to-volume ratio of small particles.

[8] Solid phases, typically with different crystal structures, are designated by lower case Greek letters. The sequence of letters tends to follow their appearance in a phase diagram, or their sequence of discovery.

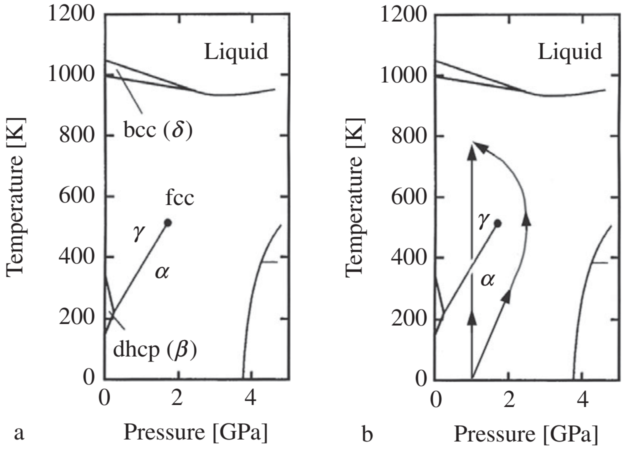

Figure 1.3 (**a**) Low-pressure region of the cerium *T–P* phase diagram. The solid phases at zero pressure are fcc α, double hcp β, fcc γ, bcc δ. (**b**) Two paths through the phase diagram of part a. One path has a discontinuous expansion of the fcc unit cell, the other a continuous expansion.

temperature, the α-phase undergoes a sudden expansion of its fcc unit cell as it transforms into the γ-phase. The how and why of this phase transition is not fully understood today, but its existence is not in doubt.[9]

Obviously the crystallographic symmetries of two fcc phases are the same, even if they differ in the sizes of their unit cells. With such a special relationship, we might ask if it is possible to go from one to the other in a continuous way, without a discontinuous change in volume. It turns out that this is indeed possible for cerium beyond a pressure of 2 GPa and a temperature of 500 K. The *T–P* phase diagram of cerium metal has a "critical point," beyond which the two fcc phases are indistinguishable. It is possible to change from a first-order discontinuous phase transition at lower pressures (or temperatures) to a second-order continuous phase transition by taking a path around the critical point in the phase diagram. If we start at $T = 0$ K, $P = 1$ GPa, and go up in temperature and pressure along a curved path that goes to the right of the critical point in Fig. 1.3b, the volume of the fcc unit cell will expand continuously.

It is perhaps better known that the *T–P* phase diagram of water has a critical point, beyond which the liquid and gas phases become indistinguishable.[10] Evidently there can be a symmetry relationship between atom arrangements in gases and liquids that allows such continuous transitions.

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[9] Cerium is the first element on the periodic table with an f-electron, and its electronic structure is a challenge to understand today. Its fcc–fcc transformation has attracted considerable attention, in part because of suggestions that its outer electrons become delocalized when the γ-phase collapses into the high-density α-phase.

[10] Carbon dioxide also has a well-known critical point of its liquid and gas phases. When pushed beyond the critical point, "supercritical" carbon dioxide is an effective agent for dry cleaning clothes.