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Phase Transitions in Materials

Offering a fresh viewpoint on phase changes and the thermodynamics of materials, this textbook covers the thermodynamics and kinetics of the most important phase transitions in materials science, spanning classical metallurgy through to nanoscience and quantum phase transitions.

Clear, concise, and complete explanations rigorously address transitions from the atomic scale up, providing the quantitative concepts, analytical tools, and methods needed to understand modern research in materials science. Topics are grouped according to complexity, ensuring that students have a solid grounding in core topics before they begin to tackle more advanced material, and are accompanied by numerous end-of-chapter problems.

With explanations firmly rooted in the context of modern advances in electronic structure and statistical mechanics, and developed from classroom teaching, this book is the ideal companion for graduate students and researchers in materials science, condensed matter physics, solid state science, and physical chemistry.

Brent Fultz is the Barbara and Stanley R. Rawn, Jr., Professor of Materials Science and Applied Physics at the California Institute of Technology. He has been awarded a Presidential Young Investigator Award, the EMPMD Distinguished Scientist Award (2010), and has led large projects such as the state-of-the-art neutron scattering instrument, ARCS, and data analysis for neutron scattering experiments, DANSE.

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BRENT FULTZ
California Institute of Technology

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This book is dedicated to Emily, Eric, and Elissa

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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 linear 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, the statistical mechanics of atom arrangements on a lattice is developed. The approach uses a minimum amount of information about interatomic interactions, avoiding detailed issues at the level of electrons. Statistical mechanics on an Ising lattice is used to understand alloy phase stability for basic behaviors of chemical unmixing and ordering transitions. This approach illustrates key concepts of equilibrium T–c phase diagrams, and is extended to explain some kinetic processes. Essentials of diffusion, nucleation, and their effects on kinetics are covered in Part I.

Part II addresses the origins of materials thermodynamics and kinetics at the level of atoms and electrons. Electronic and elastic energy are covered, and the different types of entropy, especially configurational and vibrational, are presented in the context of phase transitions. Effects of pressure, combined with temperature, are explained with a few concepts of chemical bonding. The kinetics of atom movements are developed for diffusion in solids, and from the statistical kinetics of the atom–vacancy interchange.

Part III is the largest. It describes many of the important phase transformations in materials, with the concepts used to understand them. Topics include melting, phase transformations by nucleation and growth, spinodal decomposition, freezing and phase fields, continuous ordering, martensitic transformations, phenomena in nanomaterials, phase transitions involving electrons or spins, and quantum phase transitions. These different phase transitions in materials are covered at different breadths and depths based on their richness or importance, although this reflects my own bias. Many topics from metallurgy and ceramic engineering are covered, although the connection between processing and

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

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properties is less emphasized, allowing for a more concise presentation than in traditional texts. Part III includes a number of topics from condensed matter physics that were selected in part because they give new insights into materials phenomena.

Part IV presents topics that are more modern, but have proved their importance. Low- and high-temperature treatments of the partition function, the renormalization group, scaling theory, a k-space formulation of elastic energy, nonequilibrium states in crystalline alloys, fluctuations and dissipation, and some complexities of high-temperature thermodynamics are presented. The topics in Part IV are explained at a fundamental level, but unlike Parts I through III, for conciseness in Part IV there are some omissions of methods and steps.

The book draws a distinction between phase transformations and phase transitions. Phase transitions are thermodynamic phenomena based on free energy alone, whereas phase transformations include kinetic processes that alter the life cycle of the phase change. Phase transitions originate from discontinuities in free energy functions, so much of the text focuses on formulating free energies for different systems. The free energy is often formulated with models based on statistical mechanics. The Ising model proves a reliable workhorse, offering methods and results that are useful for many different phase transitions in materials. Other topics that recur in the text are Landau theory in various forms, the topic of domains, the square gradient energy, the effect of curvature on nucleation, and dynamics with the kinetic master equation. Sometimes the thermodynamics of phase transitions is developed with the partition function, although the classical equation $G = E - TS + PV$ is used widely, and it is assumed that the reader has some familiarity with the terms in this expression. For the kinetics of phase transformations, there is some traditional presentation of diffusion and nucleation, but the kinetic master equation is also used throughout the text.

Many topics in phase transitions and related phenomena are not covered in this text. These include: other mechanisms of atom movements (and their effects on kinetics), polymer flow and dynamics including reptation, phase transitions in fluid systems including phenomena near the critical temperature, 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 extensions to phenomena at finite temperatures.

The field of phase transitions is huge, and continues to grow. This text is a snapshot of phase transitions in materials in the year 2013, composed from the angle of the author. 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 many core topics will remain the same – the free energy of materials will remain the central concept, surrounded by issues of kinetics.

Teaching

I use this text for a graduate-level course taken by Ph.D. students in both materials science and in applied physics at the California Institute of Technology. The 10-week course, which

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includes approximately 30 hours of classroom lectures, 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 familiar with the use of the partition function to obtain thermodynamic quantities, and have seen basic concepts from quantum statistical mechanics such as the Fermi–Dirac distribution. Familiarity with some concepts from solid-state physics and chemistry is certainly helpful, as is prior exposure to diffusion and transport, but the text develops many of the important concepts as needed.

In the one-quarter graduate-level course at Caltech, I cover all topics in Parts I and II, moving in sequence through these chapters. Time limitations force a selection of topics from Parts III and IV, but I typically cover more of Part III than Part IV. For example, this year I covered Chapters 10, 11, 12, parts of 13, 15, 16, 19, and selections from 20, 22, 24. It may be unrealistic to cover all the content in the book in a 15-week semester with 45 hours of lectures. An instructor can certainly exercise discretion in selecting topics for the second half of his or her course.

Most of the problems at the end of each chapter have been used for weekly student assignments, and this experience has helped to improve their wording and content. The majority of these problems make use of concepts explained in the text, fill in the explanations of concepts, or extend analyses. Others develop new concepts not described in the chapter, but these problems usually include longer explanations and hints that may be worth reading even without working the problem. None of the problems is intended to be particularly difficult, and some can be answered quickly once the main idea emerges. I usually assign five or six problems every week during the term. An expanding 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 this book. Jeff has since published a fine book on phase transformations in materials that is available at low cost from McMaster Innovation Press.

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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	speed of sound or light
c_{A}	concentration of A-atoms
c_{A}	weight of atomic wavefunction on atom A in a molecular wave function
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_0	prefactor for exponential form of diffusion coefficient

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$\tilde{D}(c)$	interdiffusion coefficient
$\underline{D}(\vec{k})$, $D_{ij}(\vec{k})$	dynamical matrix, element of
δ	relative change in radius (of misfitting sphere)
$\Delta G_{\rm V}$	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 B-atom
$e_{\rm R}$, $e_{\rm W}$	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
$E_{\rm el}$	elastic energy
ϵ	energy, energy of electron
ϵ	fractional difference in T from $T_{\rm c}$
ε	energy, energy of phonon
$\epsilon_{\rm F}$	Fermi energy
ϵ_j, ϵ_{ij}	strain
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
γ	coefficient for linear electronic heat capacity vs. T
γ	Grüneisen parameter
γ_j	Grüneisen parameter for phonon mode j
γ_{xy}	shear strain
grad(c) or $\overrightarrow{\nabla c}$	gradient (of concentration)
G	Gibbs free energy
$G(\vec{r},t)$	Van Hove space-time correlation function
Γ	atomic jump frequency
Γ	point at origin of reciprocal lattice
h	bond integral
$\hbar$	Planck's constant divided by 2π
H	Hamiltonian

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$\vec{j}$	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)
$\vec{J}_A$	flux of A-atoms
$J(\vec{r}_1 - \vec{r}_j)$	magnetic exchange energy
k	partitioning ratio $k = c_s/c_l$
$\vec{k}$	wavevector
k_B	Boltzmann's constant
κ_s, κ_l	thermal conductivity of solid and liquid
κ	coefficient for square gradient energy
κ	Ginzburg–Landau parameter
L	latent heat
L	long-range order parameter
LHS	left-hand side
λ	wavelength
λ	electron–phonon coupling parameter
m	mass
M	mobility
$\mathcal{M}$	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)
$N_{AB}^{\alpha\beta}$	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
η	fractional change of lattice parameter with composition
η	order parameter
p_i	probability of a state
$\vec{p}$	momentum
p_A	partial pressure of vapor of element A

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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)
P	Péclet number
$\Phi(r)$	interatomic, central-force potential
$\Phi_{\mathrm{M}}(r)$, $\Phi_{\mathrm{L-J}}(r)$	Morse potential, Lennard–Jones potential
Φ_0	quantum of magnetic flux $hc/2e$
Q	compositional wavevector $2\pi/\lambda$
$\vec{Q}$	momentum transfer in scattering
$\mathcal{Q}$	quality factor of damped harmonic oscillator
$\theta(\vec{r})$	Heaviside function, 1 in the region, 0 outside
$\theta(\vec{r},t)$	phase of wavefunction in space and time
Θ_{D}	Debye temperature
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
$\rho(\epsilon_{\mathrm{F}})$	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

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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)
$\vec{u}(x, y, z)$	displacement vector
U	difference in chemical preferences of A- and B-atoms $U = (e_{\mathrm{AA}} - e_{\mathrm{BB}})/4V$
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
W	the 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
ω	angular frequency
Ω	number of states accessible to the system
Ω	atomic volume
Ω_j	configurations of a system with energy j
ξ	correlation function
ξ	length
$\{\chi_i\}$	reaction coordinates
χ	susceptibility

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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

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