

A Guide to the Theory of Condensed Matter

A Guide to the Theory of Condensed Matter

By

Marian Apostol

**Cambridge
Scholars
Publishing**



A Guide to the Theory of Condensed Matter

By Marian Apostol

This book first published 2026

Cambridge Scholars Publishing

Lady Stephenson Library, Newcastle upon Tyne, NE6 2PA, UK

British Library Cataloguing in Publication Data

A catalogue record for this book is available from the British Library

Copyright © 2026 by Marian Apostol

All rights for this book reserved. No part of this book may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, without the prior permission of the copyright owner.

ISBN: 978-1-0364-7298-6

ISBN (Ebook): 978-1-0364-7299-3

Contents

1	Foreword	1
2	Basic Notions	3
3	Cohesion and Structure	7
3.1	London-van der Waals forces	7
3.2	Madelung energy	8
3.3	Cohesion	9
3.4	Unit cell. Translation symmetry	10
3.5	Crystalline symmetry	12
3.6	Defects	14
3.7	Concluding remarks	14
4	Phonons	15
4.1	Elasticity	15
4.2	Thermo-elastic coupling	17
4.3	Sound waves	18
4.4	Elasticity of crystals	19
4.5	Lattice vibrations	20
4.6	van Hove singularities	21
4.7	Phonons	22
4.8	Heat capacity	24
4.9	Debye interpolation	25
4.10	Thermal expansion	26
4.11	Low-dimensional solids	27
4.12	Phonon thermoconductivity	29
4.13	Concluding remarks	31
5	X-Rays Diffraction	33
5.1	Elastic scattering of X-rays	33

Contents

5.2	Diffraction peaks in crystals	34
5.3	Average total intensity	37
5.4	Diffuse thermal scattering of <i>X</i> -rays	39
5.5	Lattice distortion and phase defects	40
5.6	<i>X</i> -rays scattering and phonons	42
5.7	Higher-order effects	45
5.8	Concluding remarks	47
6	Electrons	49
6.1	Free electrons	49
6.2	Thermal properties	51
6.3	Screening and cohesion	53
6.4	Energy bands	57
6.5	Plasmons	62
6.6	Longitudinal sound	63
6.7	Electron-phonon interaction	64
6.8	Pairing interaction	68
6.9	Sound absorption	69
6.10	Electron thermoconductivity	70
6.11	Electrical conductivity	71
6.12	Thermopower	72
6.13	Hall effect	73
6.14	Onsager's orbits	75
6.15	Magnetic oscillations	77
6.16	Concluding remarks	79
7	Semiconductors	81
7.1	Introduction	81
7.2	The law of mass action	82
7.3	Transport	83
7.4	Transport coefficients	84
7.5	Impurity states	87
7.6	Surfaces	87
7.7	Hall effect	89
7.8	Semiconducting devices	90
7.9	Concluding remarks	91

Contents

8	Electricity in Matter	93
8.1	Electric field in conductors	93
8.2	Dielectrics	95
8.3	Thermodynamics of dielectrics	98
8.4	Electrostriction	99
8.5	Crystalline dielectrics	99
8.6	Piezoelectrics	100
8.7	Ferroelectrics	101
8.8	Magnetic bodies	103
8.9	Thermodynamics of magnetic bodies	106
8.10	Concluding remarks	107
9	Electromagnetic Phenomena in Matter	109
9.1	Introduction	109
9.2	Plasmons	112
9.3	Thomas-Fermi screening	114
9.4	Polaritons	115
9.5	Effects of interaction	117
9.6	Optical spectroscopy	118
9.7	Excitons	121
9.8	Other optical effects	122
9.9	Concluding remarks	122
10	Magnetism, 1	123
10.1	Paramagnetism	123
10.2	Weiss molecular field	124
10.3	Quantum magnetism	124
10.4	Exchange energy	126
10.5	Magnetic models	127
10.6	Below the Curie temperature	127
10.7	Larmor's precession	128
10.8	Spin waves. Magnons	129
11	Magnetism, 2	133
11.1	Ferromagnetic domains	133
11.2	Applied magnetism	134
11.3	Ferrimagnetism and antiferromagnetism	135
11.4	Pauli paramagnetism	136

Contents

11.5 Landau diamagnetism	137
11.6 Langevin diamagnetism	139
11.7 van Vleck paramagnetism	139
11.8 Electronic ferromagnetism	140
11.9 Concluding remarks	141
12 Magnetic Resonance	143
12.1 Larmor equation	143
12.2 Bloch equations	144
12.3 Motional narrowing	145
12.4 Hyperfine splitting	146
12.5 Paramagnetic defects	146
12.6 Knight shift	147
12.7 Nuclear quadrupole resonance	147
12.8 Ferromagnetic (antiferromagnetic) resonance	148
12.9 Concluding remarks	149
13 Disorder	151
13.1 Introduction	151
13.2 Central peak	151
13.3 Glass viscosity	152
13.4 Excitations in disordered matter	153
13.5 Point-like defects	153
13.6 Alloys	154
13.7 Order-disorder transition	155
13.8 Concluding remarks	156
14 Superconductivity, 1	157
14.1 Introduction	157
14.2 Cooper pair	158
14.3 BCS theory	159
14.4 Gap equation and critical temperature	161
14.5 Thermal properties	162
14.6 Acoustic attenuation	164
14.7 Microwave absorption	165
14.8 Nuclear spin relaxation rate	166
14.9 Electron tunneling	166

Contents

15 Superconductivity, 2	169
15.1 Josephson current	169
15.2 Ginsburg-Landau theory and phase transition	170
15.3 Meissner effect	172
15.4 Flux quantization	173
15.5 Coherence length	174
15.6 Surface energy	174
15.7 Miscellanea	175
15.8 Andreev reflection	177
15.9 Concluding remarks	179
16 Addendum: One-Dimensional Periodic Potential	181
16.1 Bloch theorem	181
16.2 Kronig-Penney potential	188
16.3 Delta potential	193
16.4 Periodic perturbation	195
16.5 Tight-binding electrons	199
16.6 Wannier functions	202
16.7 Commensurability energy	208
Index	213

1 Foreword

This is a condensed book on *The Theory of Condensed Matter*. I was due for long to write it down. It focuses on the most fundamental things in the field. The most fundamental things are those that are sufficiently clear to be expressed mathematically with a minimum of mathematics. Most of them pertain to solid state. Particular instances of condensed matter, as well as more technical issues, are left to a presumed second part of the book. On a larger scale the Condensed Matter includes many other things, from gases and liquids to atomic nuclei and high-energy physics.¹ The Theory of Condensed Matter is Quantum Mechanics and Statistical Physics. Wherever we have a macroscopic ensemble of particles we have condensed matter. By "macroscopic" we mean much greater than unity.

The *Chapters* in this book are written as self-consistently as possible. Usually, a perfectly coherent presentation is hampered by a still lacking theory of matter cohesion and aggregation.²

A general guide of references is provided by F. Seitz, *Modern Theory of Solids*, McGraw-Hill (1940); Ch. Kittel, *Introduction to Solid State Physics*, Wiley (1996) and L. Landau and E. Lifshitz, *Course of Theoretical Physics*, especially *Statistical Physics* (vols. 5 and 9), *Electrodynamics of Continuous Media* (vol. 8) and *Physical Kinetics* (vol. 10).

¹Theory of liquids is given in M. Apostol, *Physica* **B403** 3946 (2008), *Phys.&Chem. Liquids* **47** 35 (2009), van der Waals equation for real gases is in M. Apostol, *J. Math. Theor. Phys.* **1** 215 (2018), theory of plasma, colloids and electrolytes in M. Apostol and L. C. Cune, *Phys. Lett.* **A381** 1831 (2019), *Chem. Phys.* **531** 110660 (2020), *Phys. Chem. Liquids* **60** 827 (2022), M. Apostol, *Chem. Phys.* **558** 111514 (2022); macroscopic ensembles of electron-positron pairs are described in M. Apostol, *J. Mod. Optics* **58** 611 (2011).

²Meantime this theory has been provided by L. C. Cune and M. Apostol, *Phys. Lett.* **A273** 117 (2000).

1 Foreword

Other general references of interest are Ch. Kittel, *Quantum Theory of Solids*, Pergamon (1963); J. M. Ziman, *Principles of the Theory of Solids*, Cambridge (1964); A. L. Fetter and J. D. Walecka, *Quantum Theory of Many-Particle Systems*, Dover (1973); W. Jones and N. H. March, *Theoretical Solid State Physics*, Wiley (1973); A. A. Abrikosov, L. P. Gorkov and I. E. Dzyaloshinski, *Methods of Quantum Field Theory in Statistical Physics*, Dover (1975); N. W. Ashcroft and N. D. Mermin, *Solid State Physics*, Harcourt (1976); A. Davydov, *Theorie du Solide*, Mir (1980); P. M. Chaikin and T. C. Lubensky, *Principles of Condensed Matter Physics*, Cambridge (1995).

Particular subjects in Condensed Matter can be found in author's books *Structure of Matter* (2019), *Topics in Theoretical Physics* (2024), Nova, NY; and *Physical Kinetics* (2020), *Statistical Physics* (2021), Cambridge Scholars Publishing, Newcastle upon Tyne. A first edition of this book appeared at apoma, Magurele, in 2007.

I am very indebted to the late Professor A. Corciovei from the Institute of Atomic Physics, Magurele-Bucharest, who made my acquaintance with the Solid-State Physics. I am equally indebted to my coworkers, especially Dr. L. C. Cune, who worked with me along the years in this subject. Some of them are to be found in the citations included here. Also, I am particularly indebted to Mrs. Iulia Negoita, for her invaluable help with technical matters.

This book is dedicated to my Mother, who put me on an intellectual course from my very beginning.

M. Apostol

A handwritten signature in black ink that reads "M Apostol". The letters are cursive and somewhat stylized, with the "M" being particularly prominent.

Magurele, May 2025

2 Basic Notions

Solid matter was studied in the 19th century by metallurgy, crystallography, elasticity, electricity and magnetism. The birth of solid-state physics was probably in 1912, when M. von Laue explained the diffraction of the X -rays on a crystalline lattice. The inter-atomic distances in condensed matter are of the order of a few Angstroms, $1\text{\AA} = 10^{-8}\text{cm}$. The term "solid-state" was coined around 1940, probably by the landmark book of F. Seitz, *Modern Theory of Solids*, McGraw-Hill (1940). In the 20th century a lot of advances in the subject appeared, which enlarged appreciably the field. It has been gradually understood that statistical physics and quantum mechanics provide a unifying framework for a large diversity of subjects known today as the condensed matter physics. It contains mainly solids, liquids, plasmas, soft matter. Materials science adds greatly to this diversity.

Then, the notion of lattice vibrations appeared, introduced by M. Born in the 1910s (M. Born and K. Huang, *Dynamical Theory of Crystal Lattices*, Oxford, (1954)). These were already quantized as phonons, with typical energies from zero to $\simeq 10\text{meV}$ ($1\text{eV} = 1.6 \cdot 10^{-12}\text{erg}$), by Einstein in 1907 and P. Debye in 1912. Solids have been gradually understood as cohesive ensembles of atoms, held together by van der Waals forces (crystals of inert gases, molecular crystals), hydrogen bonds, electrons (metals), Coulomb forces (ionic crystals) and chemical bonding (covalent crystals). The cohesive energy of solids is of the order of 10meV to a few eV s per atom. The aggregation of matter is still an incipient problem today.

A major breakthrough came in 1927, when M. Born and R. J. Oppenheimer showed that electrons can be decoupled from atoms, by virtue of the small mass ratio $m/M \simeq 10^{-5}$ ($m \simeq 10^{-27}\text{g}$ is the electron mass and M denotes the atomic mass; the nucleon mass is $\simeq 2000$

2 Basic Notions

electronic mass). Electrons in metals may then be viewed as a gas giving rise to electrical and thermal conductivity, according to a classical theory by P. Drude and H. A. Lorentz in the first decade of the 20th century (H. A. Lorentz, *The Theory of Electrons*, Dover (1902)). Another major breakthrough came in 1928, when F. Bloch introduced the notion of electron energy bands, as a result of the interaction of the electrons with the crystalline lattice, thus explaining the electrical conductivity, the insulators and semiconductors. Later on, the notion of Brillouin zone has been introduced. Typically, the energy bands and the energy gaps intervening in-between have an energy of the order of $\simeq 1eV$. The paramagnetism was explained in 1927 by W. Pauli, the metallic diamagnetism in 1933 by L. Landau and the molecular exchange field of the ferromagnetism in 1928 by W. Heisenberg. Then, the notion of Fermi surface appeared.

A long-standing puzzle concerning the interaction between the electrons in solids has finally been solved by the Landau theory of the normal Fermi liquid in 1956. The basic notion of the quasi-particle elementary excitation has been introduced, as well as the collective elementary excitations.

Meantime, a major advance was recorded starting in 1937 by L. Landau with the theory of the order parameter of the second-order phase transitions. Superfluidity of He^4 was explained by L. Landau in 1940, later on the superconductivity by L. Landau and V. Ginszburg, and, finally, there appeared the theory of superconductivity of J. Bardeen, L. Cooper and W. Schrieffer in 1957. The notion of quantum-statistical macroscopic condensate came along those years.

Another landmark in these developments was the book by Ch. Kittel, *Introduction to Solid State Physics*, Wiley (1953).

The second half of the 20th century was dominated by the semiconductor physics, following the discovery of the transistor in 1948 by J. Bardeen, W. Brattain and W. Shokley, *Si* electronics industry, intense research in magnetism, neutron scattering, superconductivity, optical spectroscopy, surfaces, solid-state junctions, etc. Quasi-one dimensional materials were a long-standing problem for the scientific investigation. New tools have been invented, notably magnetic resonance, electron microscopy and the atomic force microscopy. A major

2 *Basic Notions*

breakthrough was the explanation of magnetic insulators by Anderson around 1960.

Notable subjects in condensed matter physics dominated successively the research starting, say, around the 50s. They were the amorphous solids, low dimensional structures, renormalization techniques for critical exponents, soft matter, charge and spin density waves, high- T_c superconductivity (in cuprate oxides), quantum Hall effect (integral and non-integral), fullerenes, nanostructures, heavy fermions and highly-correlated fermions, giant magnetoresistance and colossal magnetoresistance, Bose-Einstein condensation, spintronics, photonics, etc.

3 Cohesion and Structure

3.1 London-van der Waals forces

Let us consider two neutral atoms (molecules). The electron motion induces in each of them a dipole momentum. The dipole \mathbf{p} in one atom creates a field $\mathbf{E} = [3(\mathbf{n}\mathbf{p})\mathbf{n} - \mathbf{p}]/R^3 = 2\mathbf{p}/R^3$ at the other atom placed at distance \mathbf{R} , where $\mathbf{n} = \mathbf{R}/R$. At the same time it induces a dipole $\mathbf{p}' = \alpha\mathbf{E} = 2\alpha\mathbf{p}/R^3$, where α is the atomic polarizability. The interaction energy is $U = -\mathbf{p}'\mathbf{E}/2 = -2\alpha p^2/R^6$. It is worth noting that it is equivalent with a second-order perturbation theory effect and it is always negative.¹ It is known as the London-van der Waals energy.² The corresponding forces are thought to ensure cohesion of crystals of inert gases and molecular solids.

With usual notations an electron under the action of an electric field E moves according to $m\ddot{x} = -eE$, which gives an amplitude $x = eE/m\omega^2$ and a polarizability $\alpha = ex/E = e^2/m\omega^2$. Introducing it in the energy given above and making use of $p = ex$ we get $U = -e^4x^2/m\omega^2R^6$, where a factor 1/2 has been introduced in order to account for the fact that the two electrons are distinct. On the other hand $m\omega^2x^2 = \hbar\omega/2$, so we get finally

$$U = -\frac{e^4}{2m^2\omega^4R^6} \cdot \hbar\omega . \quad (3.1)$$

¹First-order effects in the perturbation theory are vanishing when averaged over atomic states.

²See, for instance, H. Margenau, *Revs. Mod. Phys.* **11** 1 (1939). Similarly, the interaction between a neutral atom and an ion is $U = -ae^2/2R^4$. For forces acting between polarizable bodies (London-van der Waals and Casimir forces) we refer to M. Apostol and G. Vaman, *Progr. Electrom. Res. (PIER)* **B19** 115 (2010); *Roum. J. Phys.* **55** 764 (2010); M. Apostol, *Physica* **B409** 57 (2013).

3 Cohesion and Structure

The formula is valid in the quasi-static limit $c/\omega \gg R$, where c denotes the velocity of light. The frequency ω represents a characteristic atomic frequency, as seen for instance in the main absorption line. We recall that the electron charge is $-e = -4.8 \times 10^{-10}esu$, the electron mass is $m \simeq 10^{-27}g$ for lengths measured in cm and energy measured in erg .³ It is worth noting that the London-van der Waals energy is a purely quantum effect. It can also be written as $U = -(\alpha^2/2R^6)\hbar\omega$. Its typical values are of the order of $100K$.⁴

A convenient representation of the atomic interacting energy includes also a repulsive part besides the attractive part given by (3.1). For instance

$$U = 4\varepsilon [(\sigma/R)^{12} - (\sigma/R)^6] \quad , \quad (3.2)$$

with parameters ε and σ , is known as the Lennard-Jones potential.⁵ The summation over all lattice sites gives the total interaction (cohesive) energy. The equilibrium inter-atomic distances are of the order $R \sim \sigma$ and the cohesive energy per atom is of the order 4ε . The (bulk) modulus of compression $B = -V(\partial p/\partial V)$ can be taken approximately $B = V(\partial^2 U/\partial V^2) \sim \varepsilon/\sigma^3$.

3.2 Madelung energy

In ionic crystals (*e.g.* alkali halides) it is convenient to write the energy as

$$U = N(\lambda z e^{-R/\rho} - \alpha q^2/R) \quad , \quad (3.3)$$

where N is the number of atoms, z is the number of nearest-neighbours, q is the ionic charge and R is the inter-atomic distance. λ , ρ are parameters and α is known as the Madelung constant.⁶ The first term in the *rhs* of equation (3.3) describes a screened Coulomb repulsion and the second term corresponds to the Coulomb ionic energy. The Madelung constant is computed for various lattices, its typical values

³Planck's constant is $\hbar \simeq 10^{-27}erg \cdot s$.

⁴ $1K = 1.38 \cdot 10^{-16}erg$ (Boltzmann constant); $1eV = 1.6 \cdot 10^{-12}erg \simeq 10^4K$.

⁵See for instance J. E. Lennard-Jones and A. E. Ingham, Proc. Roy. Soc. London **A107** 636 (1925). See also M. Apostol et al, Phys. Rev. **B52** 15031 (1995).

⁶E. Madelung, Physik. Z. **19** 524 (1918).

being of the order of unity ($\alpha \sim 1$). It is convenient to perform such summations over coordination spheres in order to ensure the convergence.⁷ The bulk modulus gives access to parameter ρ . It is of the order of atomic distances $\rho \sim a_H \simeq 0.5\text{\AA}$ or even less, as expected.⁸ Parameter λ is related to equilibrium inter-atomic distances. The cohesion energy is of the order of a few eVs per atom (strong cohesion).

3.3 Cohesion

Apart from the London-van der Waals interaction, the cohesion of matter proceeds by electron transfer. The electrons can be transferred to neighbouring atoms as in ionic bonds, or they can be shared by neighbouring atoms as in covalent bond (*e.g.* C, Si, Ge),⁹ or they can be put collectively in common by all the atoms as in metallic binding. Such processes need not be totally distinct, and mixed bonds may appear usually. The semi-empirical knowledge of chemical bond has been largely organized by the concept of valency.¹⁰ The quantum treatment of cohesion and aggregation of matter encounters long-standing difficulties.¹¹ There are mainly two general approaches: the ab-initio wavefunction method¹² and the density functional method,¹³ each with its own problems. A theory of metallic binding has been given recently, as based on the quasi-classical description of the Thomas-Fermi method.¹⁴ Three basic elements are

⁷P. P. Ewald, Ann. Physik **64** 253 (1921). See also M. Apostol, J. Theor. Phys. **2** (1995).

⁸ $a_H = \hbar^2/me^2$ is the Bohr radius. ρ may be taken as a measure of the atomic radius.

⁹W. Heitler and F. London, Z. Phys. **44** 455 (1927).

¹⁰L. Pauling, *The Nature of the Chemical Bond*, Cornell (1960).

¹¹J. C. Slater, *Quantum Theory of Molecules and Solids*, McGraw-Hill (1963); J. C. Slater, *The Calculation of Molecular Orbitals*, Wiley (1979). See also E. Fermi, *Molekuele und Krystalle*, Barth (1938) (*Molecules, Crystals, and Quantum Statistics*, Benjamin, NY (1966)).

¹²See for instance J. A. Pople, Revs. Mod. Phys. **71** 1267 (1998).

¹³P. Hohenberg and W. Kohn, Phys. Rev. **136** B864 (1964); W. Kohn and L. J. Sham, Phys. Rev. **140** A1133 (1965).

¹⁴L. C. Cune and M. Apostol, Phys. Lett. **A273** 117 (2000); in *Molecular Low Dimensional and Nanostructured Materials for Advanced Applications*, eds. A. Graja et al, Kluwer, Dordrecht (2002); in *Low-Dimensional Systems*:

intertwined in such a theory, leading to cohesion: the Coulomb force, the Pauli exclusion principle and the quantum delocalization of the electrons.

Generally, the cohesion energy per atom in van der Waals solids is $\sim 10\text{meV}$, in hydrogen-bonds solids $\sim 0.1\text{eV}$, while in metals, ionic and covalent solids is of the order of a few eVs .¹⁵

3.4 Unit cell. Translation symmetry

It has been suspected for long that crystals must have two types of symmetries: a translation symmetry and a local crystalline symmetry. These suspicions have been confirmed by X -ray diffraction¹⁶ (and later by neutron diffraction, electron microscopy, scanning tunneling microscopy, atomic force microscopy, etc).

A crystal is a repetition in space of an atomic unit cell along three basic vectors \mathbf{a} , \mathbf{b} , \mathbf{c} such that any atomic position can be written as $\mathbf{R} = \boldsymbol{\rho} + n_1\mathbf{a} + n_2\mathbf{b} + n_3\mathbf{c}$ where $\boldsymbol{\rho}$ denotes the positions of the atoms inside the cell and $n_{1,2,3}$ are integers.¹⁷ The atoms inside the cell are called the basis of the unit cell and $\mathbf{r}_n = n_1\mathbf{a} + n_2\mathbf{b} + n_3\mathbf{c}$ describes what is called a Bravais (or a primitive) lattice. Obviously, it has a translational symmetry with the basic vectors \mathbf{a} , \mathbf{b} , \mathbf{c} . The solid body formed by these three vectors is called the unit cell of the lattice.

Let $f(\mathbf{r}_n)$ be a function which describes some properties of the crystal, where \mathbf{r}_n denotes the crystal sites. It can be expanded in a Fourier series as

$$f(\mathbf{r}_n) = \sum_{\mathbf{k}} f(\mathbf{k})e^{i\mathbf{k}\mathbf{r}_n} , \quad (3.4)$$

Theory, Preparation and some Applications, eds L. M. Liz-Marzan and M. Giersig, Kluwer (2003); Roum. J. Phys. **55** 913 (2010).

¹⁵It is a difference between alkali metals (s -electrons), transition metals (including d -electrons) and rare-earths (where localized f -electrons are present).

¹⁶W. Friedrich, P. Knipping and M. von Laue, Sitzungsber. der Bayerischen Akad. Wissenschaft., Math-Phys. Klasse, p. 303 (1912) (see also W. Barlow, Nature **29** 186, 205, 404 ((1883)).

¹⁷The choice of the unit cell is not necessarily unique.

3 Cohesion and Structure

where $k_1 = (2\pi/L_1)n_1$, etc, with L_1 the length of the crystal along the \mathbf{a} -vector, etc, in order to satisfy the cyclic boundary conditions on the sample. The inversion formula is

$$f(\mathbf{k}) = \frac{1}{N} \sum_{\mathbf{r}_n} f(\mathbf{r}_n) e^{-i\mathbf{k}\mathbf{r}_n} , \quad (3.5)$$

where N is the number of unit cells. We have also $\sum_{\mathbf{k}} \rightarrow [V/(2\pi)^3] \int d\mathbf{k}$.

\mathbf{k} in (3.4) is defined up to some vectors $\mathbf{g} = \mathbf{a}^*n_1 + \mathbf{b}^*n_2 + \mathbf{c}^*n_3$, called reciprocal vectors, which define a reciprocal lattice, such as $\mathbf{a}^*\mathbf{a} = 2\pi$, $\mathbf{a}^*\mathbf{b} = \mathbf{a}^*\mathbf{c} = 0$ and similar relations for the others. It is easy to see that these basic reciprocal vectors are given by

$$\mathbf{a}^* = 2\pi(\mathbf{b} \times \mathbf{c})/v , \quad \mathbf{b}^* = 2\pi(\mathbf{c} \times \mathbf{a})/v , \quad \mathbf{c}^* = 2\pi(\mathbf{a} \times \mathbf{b})/v , \quad (3.6)$$

where $v = \mathbf{a}(\mathbf{b} \times \mathbf{c})$ is the volume of the unit cell. The solid body formed by the three basic reciprocal vectors \mathbf{a}^* , \mathbf{b}^* , \mathbf{c}^* is known as the Brillouin zone.¹⁸ Its volume is $v^* = \mathbf{a}^*(\mathbf{b}^* \times \mathbf{c}^*) = (2\pi)^3/v$. All the physical vectors \mathbf{k} are limited to this Brillouin zone. Obviously it contains $v^*/[(2\pi)^3/V] = V/v = N$ vectors \mathbf{k} , *i.e.* the total number of unit cells in the sample. This translation symmetry is the basic element of the crystalline solid-state physics.

Similarly, suppose that we have a function $f(\mathbf{r})$, where \mathbf{r} is some vector in the crystal, with translation symmetry $f(\mathbf{r} + \mathbf{r}_n) = f(\mathbf{r})$. It can be expanded in reciprocal vectors

$$f(r) = \sum_{\mathbf{g}} f(\mathbf{g}) e^{i\mathbf{g}\mathbf{r}} , \quad (3.7)$$

with the inversion formula

$$f(\mathbf{g}) = \frac{1}{V} \int d\mathbf{r} \cdot f(\mathbf{r}) e^{-i\mathbf{g}\mathbf{r}} = \frac{1}{v} \int_v d\mathbf{r} \cdot f(\mathbf{r}) e^{-i\mathbf{g}\mathbf{r}} \quad (3.8)$$

and $v^{-1} \sum_{\mathbf{g}} \exp[i\mathbf{g}(\mathbf{r} - \mathbf{r}')] = (2\pi)^{-3} \int d\mathbf{g} \cdot \exp[i\mathbf{g}(\mathbf{r} - \mathbf{r}')] = \delta(\mathbf{r} - \mathbf{r}')$. In particular $\sum_{\mathbf{r}_n} \delta(\mathbf{r} - \mathbf{r}_n) = v^{-1} \sum_{\mathbf{g}} \exp(i\mathbf{g}\mathbf{r})$ and $\sum_{\mathbf{r}_n} \exp(i\mathbf{k}\mathbf{r}_n) = (2\pi)^3 v^{-1} \sum_{\mathbf{g}} \delta(\mathbf{k} - \mathbf{g})$.

¹⁸Sometimes they are generically denoted by a basic reciprocal vector \mathbf{G} .

3.5 Crystalline symmetry

The local crystalline symmetry consists of rotations and reflections. It is easy to see that the groups of crystalline symmetry (point groups) are finite, both their elements and their number, in order to fill the space with a discrete (not continuous) distribution of atoms. There are only rotations by 2π , $2\pi/2$, $2\pi/3$, $2\pi/4$ and $2\pi/6$. The corresponding axes of rotations are denoted by $C_{1,2,3,4,6}$. Rotations by angles of, say, $2\pi/5$ or $2\pi/7$ do not fill the space.¹⁹

There are 7 crystalline systems and 14 types of lattices. The most general system is triclinic (1 lattice) with the basic cell (not necessarily the unit cell) a general parallelepiped (all angles distinct, all basic vectors of distinct length). The next one is the monoclinic system (2 lattices) with two angles equal to $\pi/2$. It follows the orthorhombic system with all angles equal to $\pi/2$ (4 lattices). Then, there exists the tetragonal system (2 lattices) with two equal lengths and all angles equal to $\pi/2$. The cubic system (3 lattices) has all the lengths equal and all the angles equal to $\pi/2$. The trigonal system (1 lattice) has all the lengths equal and all angles equal but different from $\pi/2$. Finally, we have the hexagonal system (1 lattice) with two equal lengths different from the third one, two angles equal to $\pi/2$ and the third one equal to $2\pi/3$.

The lattices in each system differ from each other by having atoms arranged not only on the vertices of the basic cell but also on its faces or in the center. For instance, the cubic system has a simple cubic lattice (*sc*), a face-centered cubic lattice (*fcc*) and a body-centered cubic lattice (*bcc*).

The symmetry group of the triclinic system contains only rotations. It is denoted by C_i ($i = 1, 2, 3, 4, 6$). The monoclinic system has the symmetry C_{2h} , where h stands for a horizontal reflection plane. The orthorhombic system belongs to group D_{2h} : it has two additional horizontal rotation axes. The tetragonal system has the symmetry D_{4h} , the hexagonal one has the symmetry D_{6h} . The trigonal system

¹⁹Quasicrystals with fivefold symmetry are known (*Al-Mn* alloy), without translation symmetry (D. Levine and P. J. Steinhardt, Phys. Rev. Lett. **53** 2477 (1984); D. S. Schechtman et al, Phys. Rev. Lett. **53** 1951 (1984)).

3 Cohesion and Structure

has the symmetry D_{3d} : d stands here for reflections about vertical planes. Finally, the cubic system corresponds to the group O_h .

The symmetry groups and their own less-symmetric groups form the symmetry classes. There exist 32 symmetry classes. The total number of point groups is 230. It seems that they were identified already in 1895 by Fedorov, following work by Schoenflies in 1891 and others. The above symmetry considerations pertain to functions like atomic or charge density. In magnetic materials there are currents \mathbf{j} and the corresponding symmetries are more numerous as a consequence of the combination of the operation $\mathbf{j} \rightarrow -\mathbf{j}$ with the rest of the usual symmetry operations.

A basic point regarding the crystalline symmetry is that relevant functions must belong to the irreducible representations of the point group, *i.e.* they must transform into each other (through linear combinations) under the symmetry operations of the group.²⁰ Conveniently, we can denote such functions as $\varphi_i = \varphi_\alpha(\mathbf{k})$, where i stands for the couple $\alpha\mathbf{k}$, and then have $\varphi_i \rightarrow \sum G_{ij}\varphi_j$ under the action of any group operation G . Matrices G_{ij} represent irreducible representations of the group. Each energy level for instance corresponds to an irreducible representation of the symmetry group, whose dimension (number of independent functions) gives the degeneracy degree of that level. In particular, a symmetrically degenerate electronic state will always be split and the degeneracy lifted by a convenient distortion (and lowering of symmetry) of the crystal lattice. This is known as the Jahn-Teller effect.²¹

Let us finally note a convenient way of indexing planes in a crystal. We take the intercepts of a plane with the axes of the basic vectors, take the inverse of these numbers and then find out the set of minimal integers with the same mutual ratios as the inverse numbers. We get this way the so called the Miller indices. Particles may go through channels in the crystalline lattice along symmetry directions and the cross-section of channeling may provide information about the atomic interactions in crystals.²²

²⁰E. Wigner, *Group Theory and its Applications to the Quantum Mechanics of Atomic Spectra*, New York (1961).

²¹H. A. Jahn and E. Teller, Proc. Roy. Soc. London **A161** 220 (1937).

²²See, for instance, M. Apostol et al, Phys. Lett. **A44** 259 (1973); phys. stat.

3.6 Defects

Thermodynamically, a perfect crystal may be in the ground-state at zero temperature. However, at finite temperatures defects are frequent in crystals, even at equilibrium²³. First, we have the random packing, which may be thought as crystalline in two dimensions and random in the third direction. Large repetition units along one direction give the polytypism (for instance *SiC* has a repeat distance of 594 layers in one direction). As a related curiosity we note that *NaCd₂* has 1192 atoms per unit cell.²⁴ There exist then point-like defects like vacancies, interstitial sites, substitutions, or line defects like dislocations. Related to such disorder are the amorphous solids, glasses, alloys, etc. A nearly-periodic structure can be represented for instance by $\exp[i \cdot 2\pi n(1 + \eta)x/a]$, where a is the lattice constant and η is a small irrational fraction.

3.7 Concluding remarks

The basic books in the field are M. Born and K. Huang, *Dynamical Theory of Crystal Lattices*, Oxford (1954); Ch. Kittel, *Introduction to Solid State Physics*, Wiley (1996); L. Landau and E. Lifshitz, *Course of Theoretical Physics*, Elsevier (1980), vol. 3 (*Quantum Mechanics*), vol. 5 (*Statistical Physics*).

sol. **b67** 609 (1975).

²³See, for instance, M. Apostol et al, *Solid State Commun.* **96** 583 (1995); M. Apostol, *J. Phys. Chem.* **100** 14 835 (1996); *J. Mat. Sci. Lett.* **16** 1139 (1997); *Statistical Physics*, Cambridge Scholars Publishing, Newcastle upon Tyne (2021).

²⁴S. Samson, *Nature* **195** 259 (1962).

4 Phonons

4.1 Elasticity

In an elastic body there exists a displacement $\mathbf{r} \rightarrow \mathbf{r} + \mathbf{u}$ in positions, such as the change $dl^2 = dx_i dx_i$ in distance is given by $\delta(dl^2) = 2(\partial u_i / \partial x_j) dx_i dx_j$ or $\delta(dl^2) = 2u_{ij} dx_i dx_j$ where

$$u_{ij} = (1/2)(\partial u_i / \partial x_j + \partial u_j / \partial x_i) \quad (4.1)$$

is the strain tensor. For its principal axes $dx_i \rightarrow dx_i(1 + u_i)$ and the change in volume is $dV(u_1 + u_2 + u_3) = dV u_{ii}$; the trace u_{ii} is therefore related to a dilatation, while the off-diagonal components of the strain tensor are related to a shear deformation.

For an isotropic body the density of the elastic free energy reads

$$F = \frac{1}{2} \lambda u_{ii}^2 + \mu u_{ij}^2, \quad (4.2)$$

according to its invariance under rotations. The coefficients λ and μ are called the Lamé coefficients. Obviously, $\delta F = -\delta R$ where

$$\delta R = -(\lambda u_{ll} \delta_{ij} + 2\mu u_{ij}) \delta u_{ij} \quad (4.3)$$

is the mechanical work, or $\delta R = -\sigma_{ij} \delta u_{ij}$ and

$$\sigma_{ij} = \lambda u_{ll} \delta_{ij} + 2\mu u_{ij} \quad (4.4)$$

is the stress tensor. This is called Hooke's law. It can also be written as

$$\sigma_{ij} = (\lambda + 2\mu/3) u_{ll} \delta_{ij} + 2\mu(u_{ij} - u_{ll} \delta_{ij}/3), \quad (4.5)$$

4 Phonons

where $K = \lambda + 2\mu/3$ is the modulus of compression ($K = -V(\partial p/\partial V)_T$, at constant temperature T). The second term in equation (4.5) is a pure shear. Obviously $K, \mu > 0$. The inverse relation is given by

$$u_{ij} = (1/9K)\sigma_{ii}\delta_{ij} + (1/2\mu)(\sigma_{ij} - \sigma_{ll}\delta_{ij}/3) . \quad (4.6)$$

The total work can be written as

$$\begin{aligned} - \int dV \cdot \sigma_{ij}\delta u_{ij} &= - \int dV \cdot \sigma_{ij}(\partial\delta u_i/\partial x_j) = \\ &= \int dV \cdot (\partial\sigma_{ij}/\partial x_j)\delta u_i - \int df_j \cdot \sigma_{ij}\delta u_i , \end{aligned} \quad (4.7)$$

where one can see the volume forces

$$F_i = \partial\sigma_{ij}/\partial x_j \quad (4.8)$$

and the surface forces

$$F_i^s = -\sigma_{ij}df_j . \quad (4.9)$$

For the hydrostatic pressure p we have $\sigma_{ij} = -p\delta_{ij}$. The condition of equilibrium under the action of an external force F_i acting upon the surface df of the body is therefore $F_i = \sigma_{ij}df_j = \sigma_{ij}n_jdf$ where n_j is the unit vector of the surface.¹

We may take homogeneous deformations such as $\sigma_{ij} = 0$ except for $\sigma_{33} = p$. By (4.6) we get $u_{11} = u_{22} = (2\mu - 3K)p/18\mu K$ and $u_{33} = (\mu + 3K)p/9\mu K$. Young's modulus is defined as

$$E = p/u_{33} = 9\mu K/(3K + \mu) , \quad (4.10)$$

while the Poisson ratio is defined by

$$\sigma = -u_{11}/u_{33} = (3K - 2\mu)/2(3K + \mu) . \quad (4.11)$$

The latter may vary between -1 and $1/2$ (though, usually, it is always positive). These formulae can be inverted, so we get from (4.5)

$$\sigma_{ij} = \frac{E\sigma}{(1+\sigma)(1-2\sigma)}u_{ll}\delta_{ij} + \frac{E}{1+\sigma}u_{ij} . \quad (4.12)$$

Hence, it is easy to get the force

$$F_i = \partial\sigma_{ij}/\partial x_j = \frac{E}{2(1+\sigma)}\Delta u_i + \frac{E}{2(1+\sigma)(1-2\sigma)}\text{grad}_i \text{div} \mathbf{u} . \quad (4.13)$$

¹The torque can be calculated similarly. It reduces to the torque of the external forces acting upon the surface of the body.

4.2 Thermo-elastic coupling

With usual notations the density of the free energy is given by $dF = -SdT + \sigma_{ij}du_{ij}$ or

$$F = F_0 + \frac{1}{2}Ku_{ll}^2 + \mu(u_{ij} - u_{ll}\delta_{ij}/3)^2 , \quad (4.14)$$

by making use of (4.5). If we take into account the thermal expansion it reads

$$F = F_0 - K\alpha(T - T_0)u_{ll} + \frac{1}{2}Ku_{ll}^2 + \mu(u_{ij} - u_{ll}\delta_{ij}/3)^2 . \quad (4.15)$$

The stress tensor is now

$$\sigma_{ij} = -K\alpha(T - T_0)\delta_{ij} + Ku_{ll}\delta_{ij} + 2\mu(u_{ij} - u_{ll}\delta_{ij}/3) \quad (4.16)$$

and equilibrium requires

$$\alpha(T - T_0) = u_{ll} , \quad (4.17)$$

which tells that α is the coefficient of thermal expansion $\alpha = (\partial V/\partial T)/V$ (at constant pressure).

From (4.15) we get the entropy

$$S = S_0 + K\alpha u_{ll} , \quad (4.18)$$

so the heat due to deformations is given by

$$C_v(T - T_0) = -T_0K\alpha u_{ll} , \quad (4.19)$$

where C_v is the specific heat at constant volume. Equation (4.16) becomes

$$\begin{aligned} \sigma_{ij} &= (K^2\alpha^2T_0/C_v)u_{ll}\delta_{ij} + Ku_{ll}\delta_{ij} + 2\mu(u_{ij} - u_{ll}\delta_{ij}/3) = \\ &= K_{ad}u_{ll}\delta_{ij} + 2\mu(u_{ij} - u_{ll}\delta_{ij}/3) , \end{aligned} \quad (4.20)$$

where

$$K_{ad} = K(1 + K\alpha^2T_0/C_v) . \quad (4.21)$$

4 Phonons

It follows that K and μ can be viewed as isothermal moduli of elasticity, while K_{ad} and $\mu_{ad} = \mu$ can be viewed as adiabatic moduli of elasticity. They induce corresponding changes in moduli E and σ . Making use of $C_p - C_v = -T(\partial V/\partial T)_p^2/V(\partial V/\partial p)_T$ we get $C_p - C_v = K\alpha^2 T_0$, so we may use C_p instead of C_v in the above formulae, to the first order in α^2 .

4.3 Sound waves

Equation (4.13) gives equations of equilibrium and equations of motion for the elastic displacement. For instance, thermal forces introduced above are given by $-K\alpha grad T$, so we may have elastic deformation produced by thermal perturbations. We write equation (4.13) as $\rho \ddot{\mathbf{u}} = \mathbf{F}$ and introduce two velocities

$$v_t = \sqrt{\frac{E}{2\rho(1+\sigma)}} = \sqrt{\mu/\rho} , \tag{4.22}$$

$$v_l = \sqrt{\frac{E(1-\sigma)}{\rho(1+\sigma)(1-2\sigma)}} = \sqrt{(\lambda + 2\mu)/\rho} .$$

We have always $v_l > \sqrt{2}v_t$. Equation (4.13) becomes

$$\ddot{\mathbf{u}} = v_t^2 \Delta \mathbf{u} + (v_l^2 - v_t^2) grad div \mathbf{u} . \tag{4.23}$$

We write $\mathbf{u} = \mathbf{u}_t + \mathbf{u}_l$ with $div \mathbf{u}_t = 0$ and $curl \mathbf{u}_l = 0$ and substitute this \mathbf{u} in equation (4.23). We take div of both sides and get $div(\ddot{\mathbf{u}}_l - v_l^2 \Delta \mathbf{u}_l) = 0$, so, since $curl \mathbf{u}_l = 0$, we have $\ddot{\mathbf{u}}_l - v_l^2 \Delta \mathbf{u}_l = 0$. Similarly, by taking $curl$ of equation (4.23), we get $\ddot{\mathbf{u}}_t - v_t^2 \Delta \mathbf{u}_t = 0$. These are wave equations with spectrum (dispersion relations) $\omega^2 = v_{l,t}^2 k^2$. They are sound waves: u_l corresponds to compression waves (longitudinal waves, one polarization) and u_t corresponds to shear waves (transverse waves, two polarizations). Typical values of the sound velocity in solids are of the order of $10^3 m/s$.

4.4 Elasticity of crystals

The density of elastic free energy of a crystal reads

$$F = \frac{1}{2} \lambda_{ijkl} u_{ij} u_{kl} , \quad (4.24)$$

where λ_{ijkl} is the elastic modulus tensor (81 components). It is symmetric for $i \leftrightarrow j$ and $k \leftrightarrow l$, so we are left with 36 components. Further, it is symmetric for $ij \leftrightarrow kl$, so we are left with 21 components. It is also written as $\lambda_{\alpha\beta}$ with suffixes α, β corresponding to xx, yy, zz, yz, zx, xy (Voigt notation). Each crystalline symmetry class imposes a further reduction in the number of components of the elastic modulus tensor. For instance, the triclinic system has 21 components, but 3 of them can be taken equal to zero as corresponding to the orientation of the axes. So we are left with 18 independent components for the triclinic system. Similar reductions hold for the other classes. For instance, the cubic system has only 3 components of the elastic modulus tensor.

The coefficient of thermal expansion in crystals is a tensor α_{ij} (compare with (4.15)). The ellipsoid of its principal axes can have all the three components distinct, or only two, or it can be reduced to a sphere. In the first case the crystal is biaxial (with respect to its thermal expansion properties), in the second case it is uniaxial and in the third case it is isotropic. This last case occurs for cubic crystals.

The propagation of elastic waves in crystals is governed by equation $\rho \ddot{u}_i = \partial \sigma_{ij} / \partial x_j$ where the stress tensor is given by $\sigma_{ij} = \lambda_{ijkl} u_{kl}$. It is easy to see that this equation can be written as

$$\rho \ddot{u}_i = \lambda_{ijkl} \partial^2 u_l / \partial x_j \partial x_k . \quad (4.25)$$

We take the Fourier transform of this equation and get the secular equation

$$\det(\lambda_{ijkl} k_j k_k - \omega^2 \delta_{il}) = 0 . \quad (4.26)$$

This is a cubic equation in ω^2 , it has three $\omega^2 = \omega_i^2(\mathbf{k})$ roots. The spectrum has three branches in general. They correspond to the sound waves. From equations $(\lambda_{ijkl} k_j k_k - \omega^2 \delta_{il}) u_l = 0$ we get the polarization for each branch and each \mathbf{k} . They are mutually perpendicular for

4 Phonons

the three branches because they correspond to the principal axes of the tensor $\lambda_{ijkl}k_jk_k$. However, none of them are either purely longitudinal or purely transversal. The sound waves propagate with group velocity $\mathbf{v}_g = \partial\omega/\partial\mathbf{k}$ which differs in general from the propagation velocity of the wavevector (phase velocity). The group velocity depends on propagation direction (\mathbf{k} -direction) but not on the frequency. It is perpendicular to the surface $\omega(\mathbf{k}) = \text{const}$.

4.5 Lattice vibrations

The elasticity is valid in the long-wavelength limit and for Bravais lattices. In general we have, say, ν atoms in the unit cell (a basis), denoted by $s = 1, 2, \dots, \nu$. The displacement vector has components u_{si} for each unit cell, so we write them as $u_{si}(\mathbf{n})$ where \mathbf{n} stands for the position vector \mathbf{r}_n of the unit cell. It follows that the lagrangian of vibrations can be written as

$$L = \sum_{\mathbf{n}si} m_s \dot{u}_{si}^2(\mathbf{n})/2 - (1/2) \sum_{\mathbf{n}\mathbf{n}'ss'ij} \Lambda_{ij}^{ss'}(\mathbf{n} - \mathbf{n}') u_{si}(\mathbf{n}) u_{s'j}(\mathbf{n}') \quad (4.27)$$

where m_s denotes the mass of the s -th atom and Λ is a force matrix. The second-order expansion of the potential energy in (4.27) defines the harmonic approximation. Higher-order terms give anharmonic contributions. Matrix Λ has symmetry properties, for instance it is symmetrical in all its labels i, s, \mathbf{n} and its Fourier transform is hermitian. The translation symmetry requires $\sum_{\mathbf{n}s} \Lambda_{ij}^{ss'}(\mathbf{n}) = 0$. The equations of motion read

$$m_s \ddot{u}_{si}(\mathbf{n}) = - \sum_{\mathbf{n}'s'j} \Lambda_{ij}^{ss'}(\mathbf{n} - \mathbf{n}') u_{s'j}(\mathbf{n}') . \quad (4.28)$$

By a Fourier transformation we get

$$\sum_{s'j} \Lambda_{ij}^{ss'}(\mathbf{k}) u_{s'j}(\mathbf{k}) - m_s \omega^2 u_{si}(\mathbf{k}) = 0 . \quad (4.29)$$

This equation has 3ν branches $\omega^2 = \omega_\alpha^2(\mathbf{k})$ for the dispersion relations. Three branches correspond to the translation symmetry and