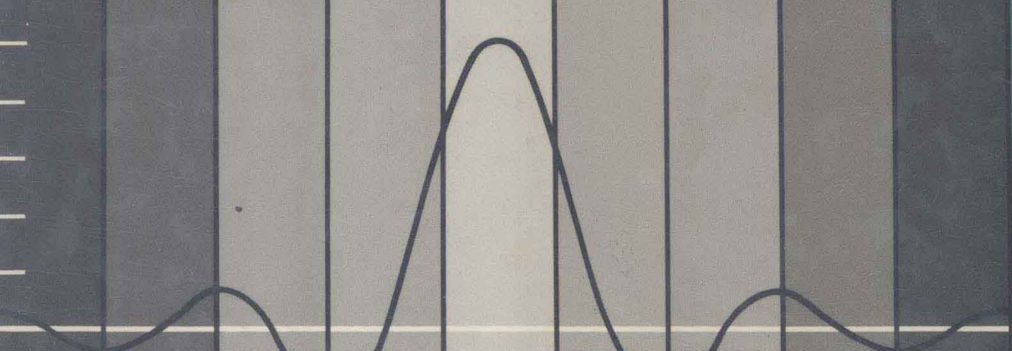
BAND THEORY OF SOLIDS: AN INTRODUCTION FROM THE POINT OF VIEW OF SYMMETRY

SIMON L. ALTMANN



Band Theory of Solids
An Introduction from the Point of View of Symmetry

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Preface

Whereas no chemist would these days treat, say, molecular vibrations without using the vocabulary of group theory, there is, unfortunately, no elementary introduction to the band theory of solids which adopts this approach. There are, of course, excellent books on the group theory of the solid state, but they are all at a rather rigorous level and are not suitable as an introduction to band theory. Almost twenty years ago I wrote such an introduction in which I made much use of the concept of symmetry, but I could not employ the vocabulary of group theory since undergraduates in the physical sciences were not exposed to this subject in those days. Finite group theory is now the *lingua franca* of chemistry and many undergraduate courses in physics include some group theory. I felt, therefore, that the time had now come to have a book which would bridge the gap between the current elementary texts on band theory and the more advanced treatments of the group theory of solid state.

I am sure I do not have to justify the use of group theory in the band theory of solids. There is hardly any subject in physics in which so much of the structure comes straight from group theory and a lot of important ideas become obscure if this language cannot be used: to have to understand band theory without realizing that the Brillouin zone is a graphical depiction of the irreducible representations of the space group of a crystal, and of the structure of their bases, is an almost intolerable limitation by present standards.

I hope that this work will not be pigeon-holed with texts on the group theory of solid state. In the present book, as a difference, only the simplest and most basic of group-theoretical ideas are used and no attempt is made at the great problems of the irreducibility and completeness of the space group representations which take so much room in the group-theoretical treatments. I have made no attempt at absolute rigour but, rather, I made a serious effort to convey a feeling for the way in which symmetry determines many of the essential ideas in solid-state theory, thus, I hope, illuminating some of the major concepts in the band theory of solids.

In writing this book I was very much aware of the present very strong interest in solid-state chemistry and it was clear to me that there was no quicker entry into the subject for chemists, with their training in the use of group theory, than by means of the approach used here. The choice of many topics was also made taking the needs of chemists into account and many of the examples used have a chemical flavour. I hope, however, that the general approach of this book will appeal to all physical scientists who would like to go a little beyond the elementary treatments so far available.

The book started as a set of lectures which I gave in 1982 at the Department of Chemistry of the University of Perugia at the invitation of Professor Antonio Sgamellotti and I am very grateful to him for having given me this opportunity. When I was a visiting professor at the Department of Chemistry in Rome (University La Sapienza) in 1985, I was presented with the possibility of greatly improving the lecture notes which I had provided at Perugia. Indeed, the typescript that was circulated at Rome contained, albeit in rudimentary form, most of the material in the present volume. I am most grateful to Professor Piero Porta who not only invited me to give those lectures but also provided numerous useful suggestions. It was my experience during these lectures that the material of this book, suitably simplified where necessary, can be covered in some twenty hours and that audiences including undergraduate students in both physics and chemistry were perfectly able to follow the material.

There is, of course, some overlap between many topics treated in this book and those in my former *Band theory of metals*. Naturally, Bloch functions and Brillouin zones have to re-appear, although the form of presentation is generally different. On the other hand, many new subjects are included. Space groups and their symmetry operations are given in some detail. There is a chapter on phonons in which the phonon spectrum of silicon is discussed as an example. The larger part of a chapter is devoted to Peierls instabilities and their relation to the Jahn–Teller effect, including a detailed treatment of quasi one-dimensional chains. A uniform treatment of Löwdin and Wannier functions is provided through a discussion of equivalent functions. A chapter on surface and impurity states contains a detailed treatment of the Koster and Slater method, as an introduction to the use of Green functions, for which a full but simple example is provided. Numerous problems throughout the book, for which complete solutions are given in its last chapter, provide an opportunity not only for applying the major ideas discussed but also for completing some parts of the treatment.

I am acutely aware, of course, not only that there are many subjects missing in this book but also that for much of the modern work in solid-state theory a different approach to the one used here is desirable. It goes without saying, for instance, that if one wants to move towards the study of bands in non-crystalline solids, the geometrical and crystallographic approach of this book is not the most useful. Likewise, in the study of many structural properties, a much more detailed study of the potential field in the solid than the one provided here is necessary. Many properties of some solids are best understood from a far more chemical point of view, and so on. I took the view, however, that what is done extremely well in other books there was no point for me to emulate. I did try instead to take a very central and significant part of the subject and then to treat it in a way that would not be easy to find in the literature. I hope that with the firm basis provided by this book readers will find it much easier to move forward in the subject.

Many kind friends have helped me to improve this book and I am most grateful to them. Through the kind intervention of Dr Graham Richards, Mr Jonathan Essex checked my approximate calculations for eqn (**14**-2.12). I am particularly indebted to Professor Roald Hoffmann who not only provided me with a critical reading of the manuscript but also arranged for two of his collaborators at Cornell, Dr Christian Kollmar and Mr Yat-Ting, to do the same. Their critical comments were enormously useful in improving the text. Drs Harry Rosenberg and Terry Willis read selected chapters and I am sure that it is thanks to them that, amongst other things, my crystallographic terminology was greatly improved. Dr Peter Herzig, of the University of Vienna, read the whole text and his critical eye spotted a number of mistakes that would have certainly made the book more difficult to read. Finally, I can hardly thank sufficiently Dr Tony Cox who read the manuscript not just once but twice and who never failed to find weak arguments in need of improvement.

In order to save on the cost of the book I have drawn all the illustrations myself on a Macintosh computer and I am very grateful to my sons, Drs Daniel and Paul Altmann for their help and advice with the necessary software.

An author is indeed fortunate who has such good friends to help him improve his work. I only hope that my readers will also approach this book in the spirit in which I wrote it. It is harder, in my experience, to provide persuasive rather than complete and rigorous argument and the reader would probably do better in trying to grasp the gist of the discussions presented here rather than attempting to analyse them to exhaustion. Within these limits, nevertheless, I have tried to make my arguments as easy to follow as possible, partly by providing a very comprehensive cross-referencing system. I have also attempted to foresee possible misreadings and I have given here and there warnings to that effect. Where I may have failed, however, it is not for want of trying!

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Notation

1. References

General cross-references

§**3**-5	Section 5 of Chapter **3**. Chapters are numbered with bold-face numerals which are dropped in all cross-references, formulae, etc. corresponding to the current chapter.
§5	Section 5 of the current chapter.
(**6**-3.5)	equation (5) of §**6**-3.
(3.5)	equation 5 of §3 of the current chapter.
(5)	equation 5 of the current section.
(L3), (R3)	left-hand side and right-hand side, respectively, of eqn (3).
2.1	after Problem, Fig., or Table, refers to the corresponding item serially numbered in Section 2. The section number is dropped within the current section.

Cross-references on left margins of displayed formulae

3	equation (3) is used to derive the equation on the right.
3′	equation (3), in a changed notation, is used to derive the equation on the right.
,3	equation (3) is used, but not immediately, to derive the equation on the right.
2,3	equations (2) and (3) are applied in that order to obtain the equation on the right.
2|3	equation (2) applied on equation (3) gives the equation on the right.
F, T, P	on any of the above, indicate a Figure, Table, or Problem, respectively.

Literature references

Ono (1945)	identifies a paper or book under that name in the alphabetic list of references at the end of the book.

2. Symbols used

A', (A'')	one-dimensional irreducible representations of a point group symmetrical (antisymmetrical) with respect to a symmetry plane, §**6**-4.
$\mathbb{A}$	some arbitrary operator.
$\forall$	for all.
$\mathbf{a}, \mathbf{b}, \mathbf{c}$	unit vectors, mostly chosen to be primitive vectors.
$\mathbf{a}^{\#}, \mathbf{b}^{\#}, \mathbf{c}^{\#}$	reciprocal vectors, (**4**-2.6), (**4**-2.7); (**4**-3.3).
a^*, $\mathbf{a}^*$	complex conjugates. *Notice that in order to avoid confusion, the asterisk is never used in this book to denote reciprocal vectors.*
α	Coulomb integral, (**14**-2.1).
$\mathscr{B}$	Bravais lattice, §**3**-5.
β	resonance integral, (**10**-2.15), (**14**-2.2).
$C(g_i)$	class of the element g_i, §**2**-1.
$\|C(G)\|$	number of classes in G, §**15**-2, Problem 2.
$\mathscr{C}$	electron concentration per atom, §**12**-1.
$\chi(g\|u)$	character of operation g in the basis $\langle u\|$, (**12**-4.1).
$\chi(\mathring{g}\|\hat{G})$	character of the operation $\mathring{g}$ (written as g when unambiguous) in the representation $\hat{G}$ of the group G, (**2**-4.17).
D	interplanar distance between planes of a stack, §**4**-4.
$\det A$	determinant of the matrix A.
$\Delta\alpha$	perturbation potential at a lattice site, §**14**-3.
$\Delta\mathscr{E}$	band gap, §**10**-1.
δ_{ij}, $\delta(\mathbf{g}, \mathbf{g}')$	Kronecker's delta, (**2**-5.2), (**4**-9.10).
δ	distortion parameter for a linear lattice, §**12**-2.
$\boldsymbol{\delta}$	distortion vector for a linear lattice, §**12**-2.
$\partial E/\partial \mathbf{k}_{\mathbf{n}}$	derivative of the energy with respect to $\mathbf{k}$ for $\mathbf{k}$ varying along $\mathbf{n}$ normal to a Brillouin zone face, §**8**-2.
E	energy.
e, E	identity element of a group, (**2**-1.3)
$\mathscr{E}$	electric field.
E_0	eigenvalue of an atomic orbital at a given site, (**10**-2.17).
E_{F}	Fermi energy, §**1**-4.
E_T	total electronic energy, (**1**-6.7).
$E^j(\mathbf{k})$	energy as a function of $\mathbf{k}$ for the j-th band, §**6**-4.
e	electron charge.
$\varepsilon_{\mathbf{q}}$	translation eigenvalues labelled by the N discrete propagation vectors $\mathbf{q}$ in the Brillouin zone, (**11**-2.16).
$\in$	belongs to.
$\phi_{\mathbf{t}}(\mathbf{r})$	atomic orbitals, §**13**-3.

φ, $\varphi(\mathbf{r})$	momentum eigenfunction, (**1**-3.3), (**1**-3.13).
$\varphi_{\mathbf{k}}(\mathbf{r})$	momentum eigenfunction in a more complete notation, (**1**-8.1); free-electron waves.
φ_i	equivalent functions, (**13**-1.8).
$\varphi_{\mathbf{t}}(\mathbf{r})$	Wannier functions, (**13**-2.1); Löwdin orbitals, § **13**-3.
G	group of operations g; a space group.
$\|G\|$	order (number of elements) of G, (**15**-2.4).
$G(E)_{pm}$	Green function, (**14**-3.17).
$\hat{G}(\mathring{g})$, $\hat{G}(g)$	matrix representative of the operator $\mathring{g}$ (written as g when unambiguous), (**2**-4.5).
${}^{i}\hat{G}$	i-th irreducible representation of G, § **15**-2, Problem 2.
$\|{}^{i}\hat{G}\|$	dimension of the above, § **15**-2, Problem 2.
g	configuration space operator, § **2**-2.
$\mathring{g}$	function space operator, written as g when unambiguous, (**2**-2.7).
g_i^{-1}	inverse of element g_i, (**2**-1.4).
$\mathbf{g}$	vector *of* the reciprocal lattice, (**4**-2.10), (**4**-6.4).
$\mathrm{grad}_{\mathbf{k}}$	gradient in **k** space, (**8**-3.1).
Γ	centre of the Brillouin zone.
γ	resonance integral, (**14**-2.3).
γ	glide plane, (**12**-3.1).
$H \subset G$	H is a subgroup of G, (**2**-1.5).
$H \lhd G$	H is an invariant subgroup of G, (**2**-1.6).
$\mathbb{H}$	quantum mechanical Hamiltonian.
$\mathit{\mathbb{H}}$	pseudo Hamiltonian, (**10**-4.6).
$\mathit{\mathbb{H}}$	Austin–Heine–Sham pseudo Hamiltonian, (**10**-4.15).
$\mathbb{H}$	perturbed Hamiltonian, (**14**-3.2).
$H_{\mathbf{kk}'}$	Hamiltonian matrix element, (**10**-1.8).
$\hbar$	Planck's constant h divided by 2π.
I	transition probability integral, (**12**-2.9).
$\|I\|$	number of irreducible representations in G, § **15**-2, Problem 2.
i	imaginary unit.
$\mathbb{i}$	inversion at the origin of coordinates.
$\mathbf{J}$	current density, (**11**-1.2).
$\mathbb{j}$	conjugator operator, (**2**-3.11).
$\mathbf{k}$	vector of orthogonal components $[k_x, k_y, k_z]$, (**1**-3.15), or more usually a vector $[k_x, k_y, k_z]^{\#}$ *in* the reciprocal lattice, (**4**-6.3).
$\|\mathbf{k}\|$	circular wave number, (**1**-8.6).
k_{B}	Boltzmann's constant.
κ	oscillator force constant, § **11**-2.
$\boldsymbol{\kappa}$	small vector normal to a Brillouin zone face, (**14**-1.9).
κ_x	integer; likewise κ_y, κ_z, (**1**-3.19).

L	length of one-dimensional crystal.
$L \otimes M$	direct product, (**2**-1.8).
λ	wave length.
m	electron mass.
μ	mass of an oscillator particle, § **11**-2.
$\boldsymbol{\mu}$	real factor of the imaginary vector $\boldsymbol{\kappa}$, § **14**-1.
N	total number of primitive cells in a crystal, (**5**-1.3); number of atoms in a piece of metal.
N_x	number of primitive cells of a crystal in the x direction, § **5**-1.
$\mathscr{N}$	electron concentration or density, § **1**-5, § **12**-1.
[illegible]	number of electrons, § **1**-4.
$\boldsymbol{N}$	normalization constant, (**15**-1-6).
$\boldsymbol{N}_{\mathbf{k}}$	normalization constant, (**13**-3.10).
n	order of the set $\{g_i\}$.
$\mathscr{n}(E)$	density of states, (**1**-5.1).
Ω	volume of the unit (primitive) cell of the crystal, (**4**-9.1).
ω	circular frequency (**1**-8.7); oscillator frequency, § **11**-2.
$\omega_{\mathbf{q}}$	normal frequency, § **11**-2.
P	point group of a space group G, § **3**-5.
$P_{\mathscr{B}}$	point group of the Bravais lattice $\mathscr{B}$, § **3**-5.
$\mathbb{P}$	projection operator, (**10**-3.10).
$\mathbf{p}$	momentum (linear).
$\mathbb{p}$	momentum operator.
$\mathbf{q}$	propagation vector with discrete values (N in number) which label vibrational states, (**11**-2.19).
$\mathbf{r}$	position vector of components $[xyz]$, (**4**-4.3); position vector *in* the lattice (**4**-1.12), (**4**-6.1).
$\boldsymbol{\rho}$	displacement vector of an atom from its equilibrium position, (**11**-2.6).
$\boldsymbol{\rho}_n$	position vector of the n-th atom of the basis, § **4**-9.
$\boldsymbol{\rho}_{\mathbf{t}}$	displacement vector corresponding to the site $\mathbf{t}$, § **11**-2.
$S_{\mathbf{kk}'}$	overlap integral, (**10**-1.9).
S	Schrödinger group, § **2**-3.
$\mathbf{s}_t$	reduced coordinates, (**11**-2.13).
$\boldsymbol{\sigma}$	electrical conductivity, conductivity tensor, (**11**-1.2).
σ	reflection plane.
σ_v, σ_d	reflection planes (vertical, that is parallel to a principal rotation axis), the σ_d planes bisecting the angle between two binary axes normal to the principal rotation axis.
$\mathbb{T}$	kinetic energy operator.
T	translation subgroup, § **3**-8.
$\lvert T \rvert$	order of the translation group T.
$\boldsymbol{T}$	kinetic energy, (**11**-2.10).

T	period (as inverse of frequency).
${}_{\mathbf{k}}\hat{T}$	**k**-th irreducible representation of the translation group T, §**5**.2.
${}_{\mathbf{k}}\hat{T}\{E\|\mathbf{t}\}$	the **k**-th irreducible representation of $\{E\|\mathbf{t}\}$, (**5**-2.9).
${}_{k_x}\hat{T}\{E\|m\mathbf{a}\}$	the k_x irreducible representation of the translation $\{E\|m\mathbf{a}\}$, §**5**.2.
t	translation in configuration space by the translation vector **t**, (**2**-2.3); translation $\{E\|\mathbf{t}\}$, (**11**-2.16).
$\mathbf{t}$	a translation vector, in particular a translation vector of the Bravais lattice $\mathscr{B}$ or vector *of* the lattice, (**3**-8.1), (**4**-6.2).
τ	relaxation time, (**11**-1.3).
$u_{\mathbf{k}}^{j}(\mathbf{r})$	cell function in the j-th band, (**5**-6.11).
$u_{\mathbf{k}}(\mathbf{r})$	cell functions, (**5**-6.4).
$\mathbf{u}$, $\mathbf{v}$, $\mathbf{w}$	primitive vectors.
$\mathbb{V}$	potential energy operator, (**10**-1.1).
V	crystal volume, volume of a lump of a solid, (**1**-3.24).
V	potential energy, (**11**-2.11).
$V(\mathbf{r})$	crystal potential field.
$V_{\mathbf{g}}$	Fourier coefficient, (**4**-9.19).
$\mathscr{V}_{\mathbf{g}}$	structure factor, (**4**-9.26).
v	volume in **k** space occupied by one electron state, spin included, (**1**-3.25).
v'	volume in **k** space occupied by one electron state, spin not included, (**1**-3.24).
v_p	phase velocity, (**1**-8.8).
$\mathbf{v}$	fractional translation vector, (**3**-4.3).
$\mathbf{v}$	velocity, §**11**-1 only.
$\mathbf{v}_g$	group velocity, (**1**-8.14).
$\mathbb{W}$	pseudopotential, (**10**-4.8).
$\mathbf{w}$	either a translation vector **t** or a fractional translation vector, §**3**-6.
X	bisector point of one of the unit vectors of the reciprocal lattice; belongs to a Brillouin zone edge, (**6**-4.2).
ξ_i	normal coordinates, (**11**-2.4).
$\Theta(x)$	step function, (**14**-4.10).
Ψ	perturbed wave function, (**14**-3.12).
ψ	wave function.
ψ^{i}	unperturbed wave function, (**14**-3.3).
$\psi_{k}^{j}(\mathbf{r})$	Bloch function of the j-th band, (**5**-6.11).
ψ^{k}	molecular orbital (linear combination of atomic orbitals), (**14**-4.1).
$\psi_{\mathbf{k}}(\mathbf{r})$	translation eigenfunctions, (**5**-5.1); Bloch functions, (**5**-6.3), (**5**-6.9).