



INTERNATIONAL SERIES OF
MONOGRAPHS ON PHYSICS

Dynamical Theory of Crystal Lattices

Max Born and
Huang Kun

DYNAMICAL THEORY OF CRYSTAL LATTICES

BY

MAX BORN

TAIT PROFESSOR OF NATURAL PHILOSOPHY
UNIVERSITY OF EDINBURGH

AND

KUN HUANG

PROFESSOR OF PHYSICS
UNIVERSITY OF PEKING

OXFORD
AT THE CLARENDON PRESS

Oxford University Press, Walton Street, Oxford OX2 6DP

*Oxford New York Toronto
Delhi Bombay Calcutta Madras Karachi
Kuala Lumpur Singapore Hong Kong Tokyo
Nairobi Dar es Salaam Cape Town
Melbourne Auckland*

*and associated companies in
Beirut Berlin Ibadan Nicosia*

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© Oxford University Press, 1954

First published 1954

Reprinted in paperback, 1969, 1985

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British Library Cataloguing in Publication Data

Born, Max

*Dynamical theory of crystal lattices.—(The
International series of monographs on physics)*

1. Lattice dynamics

I. Title II. Huang, Kun III. Series

548'.81 QD921

ISBN 0-19-851248-1

Library of Congress Cataloging in Publication Data

Born, Max, 1882-1970.

Dynamical theory of crystal lattices.

(The International series of monographs on physics)

Bibliography: p.

Includes index.

1. Crystal lattices. I. Huang, Kun. II. Title.

*III. Series: International series of monographs on
physics (Oxford, Oxfordshire)*

QD931.B67 1985 547'.81 85-15328

ISBN 0-19-851248-1 (pbk.)

Printed in Great Britain by

St Edmundsbury Press,

Bury St Edmunds, Suffolk

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INTERNATIONAL SERIES
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PREFACE

THIS book was begun during the War, about fourteen years ago. My first book on crystals had appeared during the First World War, under the title *Dynamik der Kristallgitter* (Teubner, 1915). A few years later I was invited by Sommerfeld to write an article on the subject for the *Mathematical Encyclopaedia*. This appeared in volume v, p. 527, under the title 'Atomtheorie des festen Zustandes' and was published as a separate book (Teubner, 1923). This was two years before the discovery of quantum mechanics. A report on the situation up to the year 1933 has been published as an article in the *Handbuch der Physik* by Maria Göppert-Mayer and myself. There are several other articles in this *Handbuch* by K. F. Herzfeld, R. de W. Kronig, A. Smekal, H. G. Grimm, and H. Wolff, dealing with problems of lattice dynamics. Meanwhile several books on crystal theory have been published which take proper account of quantum mechanics. The most comprehensive is that by F. Seitz, *A Modern Theory of Solids* (McGraw-Hill, N.Y. and London, 1940); other books, for example that by N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Clarendon Press, Oxford, 1940), deal only with restricted sets of problems. Some special subjects, like the theory of specific heat, infra-red absorption, and Raman effect, have become standard chapters in general textbooks. A great number of single investigations have been published since my article in the *Encyclopaedia*.

The situation seemed to demand an attempt at a new, comprehensive presentation. But the subject has become much too large to be dealt with from all aspects. The contributions of my own school during the last few years have been mainly concerned with non-conducting materials. It seemed to be desirable to give a description of the methods and results in this field.

My plan was to start from the most general principles of quantum theory and to derive in a deductive way the structures and properties of crystals, as far as one could proceed.

I wrote a series of sections which now correspond to the backbone of the Chapters IV to VII of the present book. But with the end of the war my time was so occupied with other matters that I could not continue to write this book. It remained in my desk for several years until Dr. K. Huang, at that time an I.C.I. Fellow at Liverpool, came to work with me for the holidays. I gave him this manuscript and he

was interested in the matter. He wrote several interesting papers on crystal theory, and I suggested that he should finish the book.

He accepted this and has succeeded in his task. However, the book has become rather different from my original plans. Dr. Huang, who is convinced that science's main purpose is its social usefulness, found my plan of an abstract, deductive presentation not to his taste. Therefore, he has written some introductory chapters of a more elementary character which should be easy to understand, and which lead slowly up to the general theory of the second half of the book. He has also rewritten my original text, generalizing it in many ways, and adding new sections.

Thus the final form and the wording of this book are essentially due to Dr. Huang. I have discussed the text with him and sometimes suggested alterations. He had to depart before it was quite finished and has sent me the remaining sections from China. I have checked the whole text and added a number of pages, footnotes, and some appendixes. The latter refer mainly to the historical aspect of the theory. Huang has often referred to newer events which he has witnessed, while I, being of an older generation, remember older developments. I have tried to amend this. But anyone interested in the sources should turn to my older books.

The book is not entirely a compilation of published results. The approach to the thermodynamics of lattices was sketched by me and worked out in considerable detail by Huang. His main contribution to this section is the extension of the theory of elasticity of lattices to finite strains. I think that the formulae given here, which represent the temperature-dependence of all parameters describing elastic, pyroelectric and piezoelectric properties of dielectrics, have never been given before. The formulae look rather long and complicated, but are really simple if one takes the trouble to study them. We have not discussed them in detail, and leave this to those who wish to apply them to special cases. Other sections which are entirely due to Huang are the phenomenological treatment of dispersion in the first part, and also its detailed atomistic treatment in the second part of the book, the quantum theory of width of the infra-red lines, and many other minor matters.

It may not be superfluous to mention some branches of crystal dynamics which are not in this book. There is first the theory of metals, which is a science by itself represented in several well-known textbooks (N. F. Mott and H. Jones, *The Theory of the Properties of Metals and*

Alloys, Oxford, Clarendon Press, 1936; A. H. Wilson, *The Theory of Metals*, Cambridge University Press, 2nd ed., 1953).

Then there is the wide field known under the name of 'Order-Disorder Theories', including the theory of alloys and of ferromagnetism. Here the lattice is regarded as a rigid frame; the problem consists in finding the statistical equilibrium distribution of particles, or of properties of particles, over the fixed lattice points. This has nothing to do with the dynamics of the lattice itself, and there are several accounts in the recent literature (F. C. Nix and W. Shockley, *Rev. Mod. Phys.* **10**, 1 (1938); J. H. Wannier, *Rev. Mod. Phys.* **17**, 50 (1945); L. D. Taschick and H. M. Jones, *Phys. Rev.* **91**, 1131 (1953); particularly dealing with ferromagnetism: P. R. Weiss, *Phys. Rev.* **74**, 1493 (1948)).

Other subjects omitted from the book are the theories of scattering of X-rays, electrons, and neutrons by crystal lattices. A great part of the extended literature on these subjects is concerned with the purely geometrical problem of determining lattice structures. But there are deep and important investigations on the propagation of rays of different kinds through crystal lattices which take account of the dynamical processes involved. They are all elaborations of the original work by P. P. Ewald on the dynamics of X-ray scattering. There exist fairly recent reports on scattering of X-rays and of electrons in two books by Max von Laue (*Röntgenstrahleninterferenzen*, Akad. Verlags-Ges., Becker u. Erler, Leipzig, 1941; *Materiewellen und ihre Interferenzen*, Akad. Verlags-Ges., Leipzig, 2nd ed., 1949). These books also contain sections on the interaction of lattice vibrations and the scattered particles. We have omitted these theories from our book only with regret, as they provide the most striking empirical evidence for the dynamics of lattice vibrations as treated here. But there are comprehensive accounts of these matters which made a repetition appear superfluous. (In the *Reports on Progress of Physics* are the following articles: K. Lonsdale (X-rays, experimental), **9**, 252 (1942); M. Born (X-rays, theoretical), **9**, 294 (1942); G. E. Bacon and K. Lonsdale (neutrons), **16**, 1 (1953). Further: R. D. Lowde (neutrons), *Proc. Roy. Soc. A*, **221** (1954).)

I have to say a word about the notation. It is essentially the same as that developed in my first book and consecutive papers, but adapted to British printing usage. Our main concern was economy with letters. The experimentalists dealing with crystal structures use three letters h , k , l for the Miller indices of lattice points: what a waste! If one were to follow this procedure, each letter would have to be used with many

different meanings. Even with the greatest care, we could not completely avoid this. But we hope that we have succeeded in never using the same letter with two different meanings in any one formula. We have chosen the letters x, ξ for indicating points in real space, and y, η for points in reciprocal space. The relation between these spaces is expressed in terms of affine geometry, as is customary in general relativity. The three coordinates are always numbered 1, 2, 3 and indicated by small Greek letters used as subscripts.

The reason for my writing and signing this preface alone is not only the spatial separation from my collaborator, but my wish to make it clear that the book would never have been finished without his devoted and efficient labours. He has informed me that he is going to produce a Chinese edition.

I have to thank my former collaborator, Dr. Bhatia, for helping me in revising and checking the text and reading the proofs. Dr. J. M. Ziman, Oxford, and Dr. D. J. Hooton, Edinburgh, have given their assistance in the final corrections and proof-reading, and Dr. Hooton has produced the alphabetical index.

I am much indebted to Sir Ernest Oppenheimer and the firm Industrial Distributors, London, for financial help which made the production of this book possible.

The Clarendon Press, Oxford, has obliged me very much by following all my suggestions in preparing and printing the book.

M. B.

ACKNOWLEDGEMENTS

THE authors are grateful to the following for permission to use figures :

Professor E. A. Guggenheim for a figure from Fowler and Guggenheim, *Statistical Thermodynamics* (C.U.P.), Fig. 4.

Zeitschrift für Physik (Springer-Verlag), Figs. 1, 2, 3, 21.

Proceedings of the Royal Society, A, Figs. 8, 12, 18 *b*, 26.

Philosophical Transactions of the Royal Society, A, Figs. 10, 11, 15, 16, 17, 27.

Nature (Macmillan), Fig. 18 *a*.

Physical Review, Figs. 13, 14.

Proceedings of the Cambridge Philosophical Society, Figs. 24, 25.

Annalen der Physik (J. A. Barth), Fig. 5.

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PART I

ELEMENTARY THEORIES

I

ATOMIC FORCES

1. Theoretical considerations

CRYSTALLINE solids are distinguished from other states of matter by a periodic arrangement of the atoms; such a structure is called a crystal lattice. A precise description of the geometry of a lattice will be given later in § 22 of Chapter V. Essentially the regularity displayed by a crystal lattice is that of a three-dimensional mesh which divides space into identical parallelepipeds. Imagine a number of identical atoms placed at the intersections of such a mesh; then we have what is known as a *simple lattice* (or Bravais lattice). The interstitial parallelepipeds, which have atoms for corners, are referred to as the *elementary lattice cells*; in a simple lattice there is thus exactly one atom to each elementary cell. Now if the atoms are replaced by similarly oriented molecules, the result is a general lattice structure; clearly every cell contains as many atoms as there are in one molecule. The term molecule here describes the geometrical dispositions of the atoms and need not signify a real molecule (a group of atoms form a real molecule in a lattice only if they are more tightly bound to one another than to other atoms in the lattice).

In Appendix I, the familiar structure of the NaCl lattice is illustrated together with some other common lattice types. We note that despite the obvious cubic symmetry of the NaCl structure, the elementary cells have to be chosen as rhombohedra. The vectors \mathbf{a}_1 , \mathbf{a}_2 , \mathbf{a}_3 shown in the figure are known as the *basic vectors*, which form the edges of the elementary cells. The sites of the Na^+ ions taken by themselves form a simple lattice; the NaCl structure is, on the other hand, a general lattice, since we can pair every Na^+ ion with one of its six neighbouring Cl^- and designate the pair a 'molecule' (of course no *real* molecules exist in this case, as every ion in the lattice is similarly related to all its six neighbours).

According to the underlying atomic forces, crystalline solids are roughly classified into the following four principal types:

- (1) Ionic crystals,
- (2) van der Waals crystals,

(3) Valency crystals,

(4) Metals.

A fundamental feature distinguishes types (1) and (2) from types (3) and (4). The distinction depends on the units with which the crystals are built. In a general way, one can describe the units as being *saturated* in the two former types, and *unsaturated* in the two latter. An atom (or ion) with all its electrons in closed shells (rare gas configurations) or a chemically saturated molecule is typical of a saturated unit; on the other hand, an atom that can readily form covalent bonds is an unsaturated unit. Speaking more physically, the electronic wave functions of unsaturated units, when brought together, are liable to be drastically altered, whereas the wave functions of saturated units are not so significantly affected. This difference can be traced to the fact that, in the unsaturated units, either the lowest electronic state is degenerate, or there are energy levels close to the ground state; both cases provide scope for electronic rearrangements under slight perturbations. The treatment of the crystals formed of saturated units is simpler; one can calculate the energy of interaction approximately by the quantum-mechanical perturbation theory. One important consequence is that the interaction can be considered as essentially operating between pairs, and the total energy in the lattice is the sum of the interactions between the units taken by pairs (two-body interaction). In fact, it is mainly in connexion with these crystals, namely, the ionic and van der Waals crystals, that the elementary theories are useful.

Ionic crystals. For example let us consider the alkali halides, which are the real crystals closest to the theoretical model for ionic crystals, and let us imagine building up their ionic lattices. The alkali atoms: Na, K, Rb, Cs (Li is not considered owing to the complications caused by its small size†) have one valence electron outside the complete shells; the halogen atoms: F, Cl, Br, I, on the other hand, just lack one electron to complete the outermost shell. From the atoms we form the free ions by transferring the odd valency electrons from the alkali atoms to the halogen atoms. The free ions have the stable rare gas configurations; the sequences, Na^+ , K^+ , Rb^+ , Cs^+ and F^- , Cl^- , Br^- , I^- have the structures of the rare gas atoms, Ne, Ar, Kr, Xe. The extra stability achieved in the electronic configuration by forming the free ions from the atoms is not sufficient to offset the rise in electrostatic energy involved in separating the valence electrons from the alkali ions; this is clear from a comparison of the first ionization potentials of the alkali atoms with

† Cf. L. Pauling, *The Nature of the Chemical Bond* (2nd ed., Cornell, 1948), pp. 351–63.

the electron affinities of the halogen atoms given in Table 1. The electrostatic energy is, however, largely compensated when we next bring the ions together to form the lattice. Let us imagine the ions to be brought together in the following manner. We think of the ions as being initially arrayed in accordance with the desired lattice structure, but so far apart that their interaction is negligible. The ions are then brought together uniformly so that the same lattice structure is maintained throughout.

TABLE 1

	Na	K	Rb	Cs
Ionization potential in eV.	5.12	4.32	4.16	3.87

	F	Cl	Br	I
Electron affinity† in eV.	4.15	3.72	3.50	3.14

† See Tables 11 and 12.

We can crudely consider an ion as having a radius, beyond which the electron density is negligible. Then before the ions interpenetrate they interact like point charges $\pm e$. The electrostatic energy of a lattice of point charges cannot in general be calculated in an elementary way; the difficulty is due to the slow decrease of the Coulomb interaction with distance (long range force) which makes a direct summation procedure impossible. A general method of calculating this energy and a simpler method applicable to structures of high symmetry are described in Appendix II. Here it suffices to point out that the energy is inversely proportional to the linear dimensions of the lattice. Thus the energy per cell can be written quite generally for any ionic lattice in the alternative forms

$$-(ze)^2 \frac{\alpha'}{r} = -(ze)^2 \frac{\alpha''}{d}, \quad (1.1)$$

where ze is the smallest ionic charge in the lattice, and r, d are respectively the nearest ion-ion distance in the lattice and the lattice constant, either of which gives a measure of the lattice dimensions. α' (or α''), which is a pure number known as *Madelung's constant*, depends only on the lattice structure and was first calculated by Madelung† with reference to real crystal lattices. A table of values for α' (and α'') for some common lattice types is quoted in Appendix II. Briefly, we shall refer to the above energy as *Madelung's energy*; it is the electrostatic energy between the ions in a lattice if they are considered as point charges.

† E. Madelung, *Phys. Zeit.* **19**, 524 (1918).

Madelung's energy decreases algebraically with decreasing lattice constant and tends to contract the lattice. Its effect on the lattice can thus be described as attractive. The attraction is unopposed until the neighbouring ions begin to interpenetrate, when other forces arise. Let us consider the effect of an overlap between ions. As we have explained, owing to the particular stability of saturated units, perturbation methods for energy calculation can be used. To a first approximation, the energy is given by the average value of the Hamiltonian calculated with the wave functions of the free ions (unperturbed wave functions). An exhaustive treatment of various properties of some alkali halide lattices has been given by Löwdin† on this basis. However, we shall follow a cruder method, based on the Thomas–Fermi–Dirac statistical method, due to Lenz, Gombás, and particularly Jensen;‡ with this simpler method, it is easier to see the various factors which contribute to the resultant force.

In the statistical method, an electron density function $\rho(\mathbf{x})$ replaces the wave function; once the density function is known, the corresponding energy can be calculated. For two overlapping ions, Lenz and Jensen simply superpose the density functions of the free ions; in other words, the ions are assumed to be undeformed. This is the parallel to the wave mechanical first-order perturbation method, which does not allow for the effects of the distortions in the wave functions. In the Thomas–Fermi–Dirac method,§ the following three energy terms are considered:

- (i) The *classical Coulomb energy* of the average charge distribution, namely, $-e\rho(\mathbf{x})$ plus the nuclear charges.
- (ii) The *zero-point kinetic energy* of the electrons as required by the exclusion principle, according to which a volume h^3 in phase space can accommodate no more than two electrons, h being Planck's constant, so that states of higher momenta will be involved with an increase in electron density ρ . The average kinetic energy turns out to be proportional to $\rho^{2/3}$ and the kinetic energy per unit volume is given by

$$\frac{3^{\frac{5}{3}}h^2}{40m}\left(\frac{1}{\pi}\right)^{\frac{2}{3}}\rho^{\frac{5}{3}}, \quad (1.2)$$

where m is the mass of the electron.

† P. Löwdin, *A Theoretical Investigation into some Properties of Ionic Crystals* (Uppsala, 1948). Similar calculations for NaCl were first carried out by R. Landshoff, *Zeit. f. Phys.* **102**, 201 (1936); *Phys. Rev.* **52**, 246 (1937).

‡ W. Lenz, *Zeit. f. Phys.* **77**, 713 (1932); P. Gombás, *ibid.* **121**, 523 (1943); H. Jensen, *ibid.* **77**, 722 (1932); *ibid.* **101**, 141; **101**, 164 (1936).

§ See also P. Gombás, *Theorie und Lösungsmethoden des Mehrteilchenproblems der Wellenmechanik* (Birkhauser, Basel, 1950); for general description and other references see Gombás's book.

- (iii) The *exchange energy*, which is essentially a correction to (i). The Coulomb energy calculated classically is inaccurate in two ways. First, with the electrons represented as continuous clouds, (i) includes also the self-interaction of the charge cloud of an electron with itself. Secondly, the proper quantum-mechanical anti-symmetric wave function takes care of the fact that two electrons with parallel spins avoid close encounters; (i) takes no account of this effect. These effects can be taken into account by the addition of Dirac's exchange term:

$$-\frac{3^{\frac{4}{3}}e^2}{4}\left(\frac{1}{\pi}\right)^{\frac{1}{3}}\rho^{\frac{4}{3}} \quad (1.3)$$

per unit volume, where e is the charge of the electron.

(Gombás† has further approximately corrected for the fact that electrons of opposed spins also avoid close encounters owing to their Coulomb repulsion. This correlational effect is roughly equivalent to raising the exchange term by a fraction. For our illustrative purpose, we shall consider the Thomas–Fermi–Dirac method without this further elaboration.)

The electron density function in the statistical method is determined by the condition that the corresponding energy is a minimum. Jensen‡ has calculated the density functions for all the alkali and halogen free ions. Using these density functions, we can readily calculate the total energies of the alkali halide lattices on the basis of the energy terms (i), (ii), and (iii), if the distortions of the ions are ignored. Before the ions overlap, obviously the energies (ii) and (iii) remain the same as for free ions, but the Coulomb energy (i) now includes the additional Coulomb energy between the ions. The latter is exactly the Madelung energy, which we have already discussed. When two ions overlap, we have to consider the following:

- (a) Correction to the Madelung term so as to represent correctly the Coulomb energy (i). The term is attractive so long as neither nucleus has penetrated the other ion, for the electron cloud of either ion which has penetrated the other ion is now more strongly attracted to the other nucleus.
- (b) Correction to the zero-point energy. Let ρ_1, ρ_2 respectively denote at any point in the overlap region the original densities of the free ions. The zero-point energy corresponding to the superposed density is given by

$$\frac{3^{\frac{5}{3}}h^2}{40m}\left(\frac{1}{\pi}\right)^{\frac{2}{3}}(\rho_1 + \rho_2)^{\frac{5}{3}},$$

† Loc. cit., 1943.

‡ Loc. cit., 1936.