Thermal Vibrations in Crystallography

B. T. M. Willis

A. W. Pryor

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B. T. M. Willis
Atomic Energy Research Establishment, Harwell

A. W. Pryor
Australian Atomic Energy Commission, Lucas Heights, and Visiting Fellow, School of Mathematics and Physics Macquarie University

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Dedicated to the memory of Barrie Dawson

Preface

In the past fifteen years, the work of solid-state physicists has enormously increased our knowledge of the vibrational properties of atoms in solids. This book describes the impact of this new understanding of lattice dynamics on crystallography. Whether or not a crystallographer is concerned with the vibrational properties of a crystal, his experimental measurements always relate to atoms in thermal motion and so he must know how to account for the effect of this motion in extracting the maximum amount of information from his data. Much of our discussion is in terms of simple models of the type used in solid-state physics, but we show how ideas originating from these models may be carried over into the interpretation of the more complicated systems studied by the crystallographer. We have restricted ourselves to general points which must always be considered in carrying out diffraction work, and for this reason special topics, such as the connection between lattice vibrations and structural phase transitions, are omitted.

The book is written in three parts, of three chapters each. The first part deals with the basic theory of lattice dynamics. The traditional approach to the theory begins with the vibrations of a linear chain of point masses. We begin instead with the elements of the theory of the vibrations of an isolated molecule, and then proceed from a molecule to the Born–von Kármán treatment of a crystal by introducing the twin concepts of the Brillouin zone and of running waves in a finite but unbounded medium. The treatment of the vibrations of rigid molecules in a molecular crystal follows as a straightforward extension of the Born–von Kármán procedure. Our approach has the merit of bringing the reader immediately into contact with the real world of molecules and three-dimensional crystals.

The second part covers the influence of lattice vibrations on the interpretation of Bragg intensities. This is a subject dating back to the early years of X-ray diffraction, and yet there are a number of comparatively recent developments which warrant a new discussion. These include anharmonic effects, which are often surprisingly large and may even give rise to 'forbidden' Bragg reflections, and the use of higher cumulants and of the rigid-molecule hypothesis in crystal-structure refinements. These developments have gone hand-in-hand with the modern quest for making highly accurate intensity measurements – as required, for instance, in determining the bonding-electron distributions in solids.

The last part gives a brief survey of the thermal diffuse scattering (TDS) of X-rays and neutrons. The TDS of neutrons, usually referred to as inelastic neutron scattering, provides the principal source of experimental data on phonon dispersion relations of solids. We sketch the information about interatomic forces in crystals given by these dispersion relations; more detailed discussions are given in several new books on lattice dynamics, cited in the bibliography (p. 261). In the last chapter, we describe the correction of experimentally-measured Bragg intensities for the contribution of TDS.

The book is addressed primarily to those engaged in diffraction studies but the first part would be suitable reading for undergraduate students of physics or chemistry. Matrix methods are used throughout, and an account of the relevant matrix algebra is presented in an appendix.

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B.T.M.W.
A.W.P.

Harwell and Sydney
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Glossary of important symbols

The equation numbers in parentheses refer to the place in the text where the symbol is introduced

$\mathbf{a}_i$ $(i = 1, 2, 3)$	base vectors of direct unit cell (1.1*a*).
a, a_0	cell edge of cubic crystal.
$\lvert A(j)\rvert$	amplitude of excitation of the mode (j) of an isolated molecule (2.26)
$\lvert A(j\mathbf{q})\rvert$	amplitude of excitation of the lattice mode $(j\mathbf{q})$ of a crystal (3.17).
$\mathbf{b}_j$ $(j = 1, 2, 3)$	base vectors of reciprocal unit cell (1.3).
b_κ, b_κ^{coh}	coherent neutron scattering amplitude of atom κ (1.13).
B	isotropic B factor $(\equiv 8\pi^2\langle u^2\rangle)$ (4.72).
$\mathbf{B}(\kappa)$	3×3 matrix representing mean-square displacement of atom κ (4.54).
$\mathbf{B}^{\text{mol}}(\kappa)$	6×6 matrix representing mean-square translational–librational displacement of rigid molecule κ (6.4).
c_{11}, c_{12}, c_{44}	elastic constants of cubic crystal (3.38).
c_V	specific heat.
$\mathbf{D}$	$3n\times 3n$ dynamical matrix (3.7).
$\mathbf{D}_0$	dynamical matrix without mass-adjustment (3.10*a*).
$\mathbf{D}^{\text{mol}}$	$6n\times 6n$ dynamical matrix of molecular crystal (3.50*c*).
$\mathbf{D}_0^{\text{mol}}$	dynamical matrix of molecular crystal without mass-adjustment (3.50*a*).
$\mathbf{e}(j)$	eigenvector describing pattern of atomic displacements in an isolated molecule due to the mode (j) (2.26).
$\mathbf{e}(j\mathbf{q})$	eigenvector describing pattern of atomic displacements in a crystal due to the lattice mode $(j\mathbf{q})$ (3.13).
$\mathbf{e}^{\text{mol}}(j\mathbf{q})$	eigenvector describing pattern of molecular (translational and librational) displacements in molecular crystal due to the lattice mode $(j\mathbf{q})$ (3.51).
$\mathbf{e}(\kappa\vert j)$	polarisation vector of atom κ when vibrating in the mode (j) of an isolated molecule. The assemblage of n polarisation vectors $(\kappa = 1, 2, \ldots, n)$ constitutes the $3n$-vector $\mathbf{e}(j)$ (2.31).

$\mathbf{e}(\kappa\|j\mathbf{q})$	polarisation vector of atom κ when vibrating in the mode $(j\mathbf{q})$ of a crystal. The assemblage of n polarisation vectors $(\kappa = 1, 2, \ldots, n)$ constitutes the $3n$-vector $e(j\mathbf{q})$ (3.13).
$\mathbf{e}^{\mathrm{mol}}(\kappa\|j\mathbf{q})$	polarisation vector of molecule κ when vibrating in the lattice mode $(j\mathbf{q})$ of a crystal. The assemblage of n polarisation vectors $(\kappa = 1, 2, \ldots, n)$ constitutes the $6n$-vector $\mathbf{e}^{\mathrm{mol}}(j\mathbf{q})$.
E_j	average energy of mode (j) of isolated molecule (2.40).
$E_j(\mathbf{q})$	average energy of lattice mode $(j\mathbf{q})$ of crystal (3.17).
E_0	energy of incident X-rays (neutrons); *or* integrated intensity of Bragg scattering.
E	energy of scattered X-rays (neutrons).
$F(\mathbf{Q})$, $F(\mathbf{H})$, F_{hkl}	structure factor for Bragg scattering (1.11).
$f_\kappa(\mathbf{Q})$	X-ray scattering factor of atom κ (1.12).
$g(\nu)$, $g(\omega)$	frequency distribution function (1.20).
$g_{\mathrm{T}}(\omega)$	frequency distribution function for translational modes (6.15*a*).
$g_{\mathrm{L}}(\omega)$	frequency distribution function for librational modes (6.15*b*).
$G(j\mathbf{q})$	structure factor for first-order (one-phonon) scattering associated with lattice mode $(j\mathbf{q})$ (7.4).
$\mathbf{g}$	3×3 matrix representing metric tensor with elements $g_{ij} = \mathbf{a}_i\cdot\mathbf{a}_j$.
$\mathbf{g}^{-1}$	3×3 matrix with elements $g_{ij}^{-1} = \mathbf{b}_i\cdot\mathbf{b}_j$.
$\mathbf{H}$	vector of reciprocal lattice $(\equiv h_1\mathbf{b}_1+h_2\mathbf{b}_2+h_3\mathbf{b}_3)$ (1.4).
$h_1h_2h_3$, hkl	Miller indices.
h	Miller index; *or* Planck's constant.
$\hbar$	Planck's constant $\div 2\pi$.
$\mathbf{I}$	unit matrix (2.25).
$\mathbf{I}(\kappa)$	3×3 moment-of-inertia matrix-of-molecule κ (3.49*b*).
I_0	intensity of Bragg scattering.
$I_1, I_2, \ldots$	intensity of first-order (one-phonon), second-order (two-phonon)...scattering.
$I_1(j\mathbf{q})$	intensity of first-order scattering associated with single lattice mode $(j\mathbf{q})$ (4.22).
j	label for modes of vibration of isolated molecule containing n atoms $(j = 1, 2, \ldots, 3n)$ (2.26);

	or label for branch of dispersion relations of crystal containing n atoms per unit cell ($j = 1, 2, \ldots, 3n$) (3.13).
$(j\mathbf{q})$	lattice mode of vibration belonging to jth branch of dispersion relations and with wave vector $\mathbf{q}$.
$\mathbf{k}_0$	wave vector of incident radiation (1.8*a*).
$\mathbf{k}$	wave vector of scattered radiation (1.8*a*).
k	Miller index;
	or wave number of scattered radiation.
k_B	Boltzmann's constant (1.19).
l	Miller index;
	or label for unit cell ($l = 1, 2, \ldots, N$).
$\mathbf{L}(\kappa)$	3×3 libration matrix of rigid molecule κ (6.5*b*).
$m(\kappa)$	mass of atom κ (2.11);
	or mass of molecule κ (3.49).
$\mathbf{m}(\kappa)$	3×3 diagonal matrix of masses $m(\kappa)$ (2.17).
$\mathbf{m}$	$3n \times 3n$ diagonal mass matrix (2.16).
$\mathbf{m}^{\mathrm{mol}}$	$6n \times 6n$ matrix of molecular masses and moments of inertia (3.49*b*).
$\mathbf{M}_0$	$3n \times 3n$ dynamical matrix for the isolated molecule formed by assembling $n \times n$ force-constant matrices (2.18).
$\mathbf{M}$	mass-adjusted $\mathbf{M}_0$-matrix (2.23).
m_{n}	neutron mass.
n	number of atoms in isolated molecule (2.2);
	or number of atoms in (primitive) unit cell (3.13);
	or number of molecules in (primitive) unit cell.
$\langle n \rangle$	average quantum number of a mode of vibration of a molecule or crystal (2.43).
N	number of unit cells in crystal.
N_0	number of atoms in crystal ($= nN$).
$p_\kappa(\mathbf{u})$	probability density function of atom κ (4.45).
$\mathbf{Q}$	scattering vector (1.8).
Q	magnitude of scattering vector ($= 4\pi \sin\theta_B/\lambda$ for Bragg scattering).
$\mathbf{q}$	wave vector of lattice mode of vibration.
q	wave number of lattice mode.
$\mathbf{r}(\kappa)$	equilibrium position of atom κ with respect to origin of unit cell (1.12).
$\mathbf{r}(\kappa l)$	equilibrium position of atom κ in cell l with respect to crystal origin (3.10).
$\mathbf{r}(\kappa\alpha)$	equilibrium position of atom α in molecule κ of molecular crystal (6.7).
$\mathbf{r}(l)$	vector defining position of origin of cell l in crystal (4.2).
$\mathbf{S}(\kappa)$	3×3 translation–libration matrix of rigid molecule κ (6.5*c*).

T	absolute temperature (1.19).
T_κ	temperature factor of atom κ (4.1).
$\mathbf{T}(\kappa)$	3×3 translation matrix of rigid molecule κ (6.5*a*).
$\mathbf{u}(\kappa)$	instantaneous displacement from its equilibrium position of atom κ in isolated molecule (2.1); *or* instantaneous translational displacement from its equilibrium position of a rigid molecule κ (6.6).
$\mathbf{u}(\kappa l)$	instantaneous displacement from its equilibrium position of atom κ in cell l of crystal (3.19).
$\langle u^2 \rangle$	mean-square displacement from equilibrium position.
$\mathbf{U}_0$	$3n \times 1$ column matrix representing amplitudes of displacement of n atoms in isolated molecule due to all modes of vibration (2.15); *or* $3n \times 1$ column matrix representing amplitudes of displacement of n atoms in unit cell due to all modes of vibration (3.8).
$\mathbf{U}_0(j\mathbf{q})$	$3n \times 1$ column matrix representing amplitudes of displacement of n atoms in unit cell due to single lattice mode ($j\mathbf{q}$) (3.16).
$\mathbf{U}$	mass-adjusted $\mathbf{U}_0$-matrix (2.22).
$\mathbf{U}(j\mathbf{q})$	mass-adjusted $\mathbf{U}_0(j\mathbf{q})$-matrix.
$\mathbf{U}(\kappa)$	amplitude of displacement of atom κ from all modes of vibration of molecule (2.12).
$\mathbf{U}(\kappa \| j)$	amplitude of displacement of atom κ due to mode of vibration (j) of molecule.
$\mathbf{U}(\kappa \| j\mathbf{q})$	amplitude of displacement of atom κ due to mode of vibration ($j\mathbf{q}$) of crystal (3.2); *or* amplitude of translational displacement of molecule κ due to mode of vibration ($j\mathbf{q}$) of crystal (6.5).
$\mathbf{U}_0^{\mathrm{mol}}$	$6n \times 1$ column matrix representing amplitudes of translational and librational displacements of n molecules in the unit cell of a molecular crystal.
$\mathbf{U}_0^{\mathrm{mol}}(j\mathbf{q})$	$6n \times 1$ column matrix representing amplitudes of translational and librational displacements of n molecules in unit cell due to single lattice mode ($j\mathbf{q}$).
$\mathbf{U}^{\mathrm{mol}}$	mass-adjusted $\mathbf{U}_0^{\mathrm{mol}}$ matrix.
$\mathbf{U}^{\mathrm{mol}}(j\mathbf{q})$	mass-adjusted $\mathbf{U}_0^{\mathrm{mol}}(j\mathbf{q})$ matrix.
$\mathbf{U}^{\mathrm{mol}}(\kappa \| j\mathbf{q})$	mass-adjusted 6×1 column matrix representing amplitude of translational and librational displacement of molecule when excited by lattice mode ($j\mathbf{q}$).
v_a	volume of direct unit cell (1.1*a*).
v_b	volume of reciprocal unit cell (1.5).
V	volume of crystal (1.14);

	or potential energy of molecule (2.5);
	or potential energy of crystal (3.6).
$V_\kappa(\mathbf{u})$	single-atom potential of atom κ (5.15).
v_L	velocity of longitudinal elastic wave.
v_T	velocity of transverse elastic wave.
v_s	average sound velocity (4.103).
v_0	incident neutron velocity (4.28).
v	scattered neutron velocity (4.28).
W_κ	exponent of temperature factor (i.e. $T_\kappa \equiv \exp(-W_\kappa)$) (4.9).
α_i $(i = 1, 2, 3)$	interaxial angles of direct unit cell (1.1*b*).
α $(= 1, 2, 3)$	label for three Cartesian axes *xyz* (2.5);
	or label for atom in a molecule (6.14).
α, β, γ	elements of force-constant matrix (3.29).
$\alpha, \beta, \gamma, \delta$	force constants representing coefficients in expansion of single-atom potential $V(\mathbf{u})$ in powers of $\mathbf{u}$ (5.15).
$\alpha_j(\mathbf{q})$	angle between propagation direction and polarisation direction of lattice mode ($j\mathbf{q}$) (7.8).
β_j $(j = 1, 2, 3)$	interaxial angles of reciprocal unit cell (1.6).
$\boldsymbol{\beta}(\kappa)$	3×3 matrix representing anisotropic temperature factor of atom κ (4.64).
γ_G	Grüneisen's constant (5.1).
δ_{ij}	Kronecker delta: $\delta_{ij} = 1$ for $i = j$ $= 0$ for $i \neq j$ (1.3).
δ	Dirac delta function.
ζ	wave-vector coordinate (3.31).
2θ	scattering angle ($= 2\theta_\mathrm{B}$ for Bragg scattering).
θ_B	Bragg angle.
Θ_D	Debye temperature.
$\Theta(\kappa\vert j\mathbf{q})$	amplitude of librational displacement of molecule κ due to mode of vibration ($j\mathbf{q}$) of crystal (6.5).
$\boldsymbol{\theta}(\kappa)$	instantaneous librational displacement of rigid molecule κ from its equilibrium position (6.6).
κ	label for atom in isolated molecule (2.1);
	or label for atom in (primitive) unit cell (3.1);
	or label for molecule in (primitive) unit cell (6.3).
λ	wavelength of X-rays or neutrons (1.8*b*).
ν	frequency (1.19).
	density.
$\boldsymbol{\Phi}(\kappa\kappa')$	3×3 force-constant matrix describing interaction between atoms κ and κ' in isolated molecule (2.4).
$\boldsymbol{\Phi}\begin{pmatrix}\kappa & \kappa' \\ l & l'\end{pmatrix}$	3×3 force-constant matrix describing interaction in a crystal between atom κ in cell l and atom κ' in cell l' (3.5).

$\mathbf{\Phi}^{\mathrm{mol}}\begin{pmatrix}\kappa & \kappa' \\ l & l'\end{pmatrix}$	6×6 force- and torque-constant matrix describing interaction in a molecular crystal between molecule κ in cell l and molecule κ' in cell l'.
χ	volume coefficient of expansion (5.1).
ω	circular frequency ($\equiv 2\pi\nu$).
$\omega_j(\mathbf{q})$	circular frequency of lattice mode ($j\mathbf{q}$) (3.15).
ω_{L}	frequency of longitudinal mode.
ω_{T}	frequency of transverse mode.
ω_{D}	Debye cut-off frequency (4.106).

Contents

Part I. Theory of lattice dynamics