

2.1. Phonons

BY G. ECKOLD

2.1.1. Introduction

Interatomic interactions in crystalline solids not only determine the equilibrium atomic structure but also the possible excitations of the lattice: the motions of atoms, molecules or ions. The investigation of dynamical processes provides us with detailed information about the interatomic forces. Obviously, there are a huge variety of possible collective motions within a solid, which represents a multiparticle system with 10^{23} degrees of freedom. As long as the solid may be described by an equilibrium structure and atomic displacements from the average positions are small compared with interatomic distances, the dynamical behaviour of the lattice is essentially determined by well defined lattice vibrations or phonons. These elementary excitations of a solid are described by eigenvectors and eigenfrequencies reflecting the strength of interatomic interactions. Owing to the symmetry (space group) of the equilibrium structure there are constraints for the individual eigenvectors. In special high-symmetry cases, phonon eigenvectors can even be predicted merely on the basis of group-theoretical considerations.

This chapter is devoted to the implications of lattice symmetry on the form, *i.e.* on the eigenvectors, of lattice vibrations. We restrict ourselves to the consideration of perfect crystals and harmonic vibrations. In addition, some aspects of anharmonicity are discussed in terms of a quasi-harmonic model, yielding the connection between microscopic dynamics and macroscopic thermodynamic quantities such as thermal expansion. However, intrinsic anharmonic effects associated with the interaction of phonons, phonon damping or localized vibrations due to defects, for example, are beyond the scope of this article. In Section 2.1.2 we present the fundamentals of lattice dynamics with special emphasis on the role of the dynamical matrix. Section 2.1.3 deals with the symmetry properties of this matrix along with its eigenvectors and eigenfrequencies. Symmetry-induced degeneracies will be considered in some detail as well as compatibility relations for phonon wavevectors corresponding to points of higher symmetry within the reciprocal space. Finally, the optical selection rules for long wavelength vibrations are presented. Some examples are included in order to illustrate the theoretical results.

For a further discussion of other phenomena associated with lattice vibrations the reader is referred to the monographs of Leibfried (1955), Maradudin *et al.* (1971), Reissland (1973), Srivastava (1990) or Dove (1993).

2.1.2. Fundamentals of lattice dynamics in the harmonic approximation

2.1.2.1. Hamiltonian and equations of motion

In order to reduce the complexity of lattice dynamical considerations, we describe the crystal's periodicity by the smallest unit needed to generate the whole (infinite) lattice by translation, *i.e.* the *primitive cell*. Each individual primitive cell may be characterized by a running index l and a vector \mathbf{r}_l pointing to its origin. Let there be N atoms per cell, the equilibrium positions of which are given by

$$\mathbf{r}_{\kappa l}^o = \mathbf{r}_l + \mathbf{r}_{\kappa}^o \quad \kappa = 1, \dots, N \quad l = 1, 2, \dots, \quad (2.1.2.1)$$

\mathbf{r}_{κ}^o being the vector of the κ th atom with respect to the origin of the primitive cell (see Fig. 2.1.2.1).

The set of vectors $\mathbf{r}_{\kappa l}^o$ describes the structure of the perfect lattice. At a particular time t , however, the κ th atom within the l th primitive cell, denoted by (κl) , may be found at a position $\mathbf{r}_{\kappa l}(t)$ which differs slightly from the equilibrium position, the time-dependent displacement being

$$\mathbf{u}_{\kappa l}(t) = \mathbf{r}_{\kappa l}(t) - \mathbf{r}_{\kappa l}^o = \mathbf{r}_{\kappa l}(t) - \mathbf{r}_l - \mathbf{r}_{\kappa}^o. \quad (2.1.2.2)$$

The potential energy V of the whole crystal depends on the position vectors of all atoms,

$$V = V(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{\kappa l}, \dots), \quad (2.1.2.3)$$

and is minimal if all atoms occupy their equilibrium positions. For small displacements, it can be expanded in a Taylor series with respect to $\mathbf{u}_{\kappa l}(t)$:

$$V = V^o + \frac{1}{2} \sum_{\kappa l} \sum_{\kappa' l'} \sum_{\alpha=1}^3 \sum_{\beta=1}^3 u_{\kappa l}^{\alpha}(t) V_{\alpha\beta}(\kappa l, \kappa' l') u_{\kappa' l'}^{\beta}(t) + \dots, \quad (2.1.2.4)$$

where $u_{\kappa l}^{\alpha}(t)$ denotes the Cartesian coordinate of $\mathbf{u}_{\kappa l}(t)$ in direction α . In the *harmonic approximation*, third and higher-order terms are neglected. In order to simplify the formulae, we now drop the time argument, keeping in mind that we are always dealing with dynamical displacements. The expansion coefficients in equation (2.1.2.4) are the partial derivatives of the potential energy with respect to the atomic displacements taken at the equilibrium positions:

$$V_{\alpha\beta}(\kappa l, \kappa' l') = \left. \frac{\partial^2 V}{\partial u_{\kappa l}^{\alpha} \partial u_{\kappa' l'}^{\beta}} \right|_o. \quad (2.1.2.5)$$

Using the matrix notation

$$\mathbf{V}(\kappa l, \kappa' l') = \begin{pmatrix} V_{11}(\kappa l, \kappa' l') & V_{12}(\kappa l, \kappa' l') & V_{13}(\kappa l, \kappa' l') \\ V_{21}(\kappa l, \kappa' l') & V_{22}(\kappa l, \kappa' l') & V_{23}(\kappa l, \kappa' l') \\ V_{31}(\kappa l, \kappa' l') & V_{32}(\kappa l, \kappa' l') & V_{33}(\kappa l, \kappa' l') \end{pmatrix} \quad (2.1.2.6)$$

and dropping the constant V^o , equation (2.1.2.4) reads

$$V = \frac{1}{2} \sum_{\kappa l} \sum_{\kappa' l'} \mathbf{u}_{\kappa l} \mathbf{V}(\kappa l, \kappa' l') \mathbf{u}_{\kappa' l'} + \dots \quad (2.1.2.7)$$

The product $-\mathbf{V}(\kappa l, \kappa' l') \mathbf{u}_{\kappa' l'}$ is just the force $\mathbf{f}(\kappa l)$ acting upon atom (κl) if the atom $(\kappa' l')$ is displaced by $\mathbf{u}_{\kappa' l'}$ (Fig. 2.1.2.2). Hence, the matrix $\mathbf{V}(\kappa l, \kappa' l')$ may be regarded as a *force constant matrix* and its elements $V_{\alpha\beta}(\kappa l, \kappa' l')$ as *force constants*. These parameters may be calculated with the help of specific interaction models such as pair potentials, tensor-force models or more complicated many-body interactions.

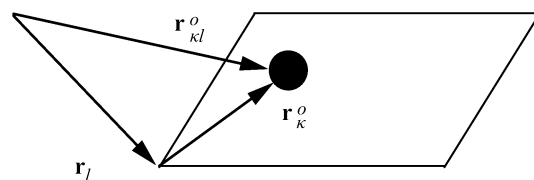


Fig. 2.1.2.1. Definition of position vectors.

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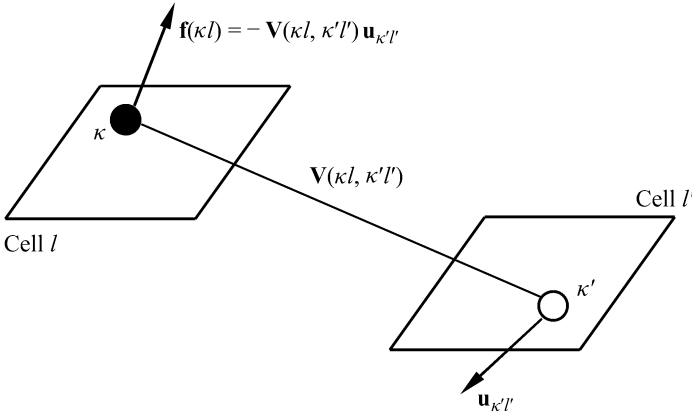


Fig. 2.1.2.2. Definition of the force acting on atom (κl) when atom $(\kappa' l')$ is displaced by $\mathbf{u}_{\kappa' l'}$.

The Hamiltonian of the perfect harmonic crystal can now be written in the form

$$H = \sum_{\kappa l} \frac{\mathbf{p}_{\kappa l}^2}{2m_{\kappa}} + \frac{1}{2} \sum_{\kappa l} \sum_{\kappa' l'} \mathbf{u}_{\kappa l} \mathbf{V}(\kappa l, \kappa' l') \mathbf{u}_{\kappa' l'} \quad (2.1.2.8)$$

if $\mathbf{p}_{\kappa l}$ and m_{κ} are the momentum and the mass of atom (κl) , respectively. Consequently, the equation of motion for a particular atom (κl) is given by

$$m_{\kappa} \frac{d^2 \mathbf{u}_{\kappa l}}{dt^2} = - \sum_{\kappa' l'} \mathbf{V}(\kappa l, \kappa' l') \mathbf{u}_{\kappa' l'}. \quad (2.1.2.9)$$

Solutions of this set of coupled differential equations are of the form

$$\mathbf{u}_{\kappa l}^{\pm} = \frac{1}{\sqrt{Nm_{\kappa}}} \mathbf{e}_{\kappa} \exp[i(\mathbf{q}\mathbf{r}_l \pm \omega t)], \quad (2.1.2.10)$$

which are plane waves with wavevector \mathbf{q} and polarization vector \mathbf{e}_{κ} . If a finite crystal is considered or if periodic boundary conditions are applied, the wavevector is restricted to a sequence of discrete and equidistant values which are, however, very close to each other. Thus, for practical work \mathbf{q} can be treated as a continuous variable. The polarization vectors \mathbf{e}_{κ} are, in general, different for every atom κ . Moreover, they depend on \mathbf{q} and for each wavevector there are $3N$ different modes of vibration characterized not only by different \mathbf{e}_{κ} 's but also by different vibrational frequencies ω . Hence, equation (2.1.2.10) can be written more specifically as

$$\mathbf{u}_{\kappa l}^{\pm}(\mathbf{q}, j) = \frac{1}{\sqrt{Nm_{\kappa}}} \mathbf{e}_{\kappa}(\mathbf{q}, j) \exp[i(\mathbf{q}\mathbf{r}_l \pm \omega_{\mathbf{q}, j} t)], \quad (2.1.2.10a)$$

where the running index $j = 1, \dots, 3N$ labels the different fundamental vibrations or *phonons*. The upper index \pm distinguishes two waves with identical frequencies which are travelling in opposite directions.

2.1.2.2. Stability conditions

Not all of the elements of the force-constant matrix are independent. From its definition, equation (2.1.2.5), it is clear that the force-constant matrix is symmetric:

$$V_{\beta\alpha}(\kappa' l', \kappa l) = V_{\alpha\beta}(\kappa l, \kappa' l'). \quad (2.1.2.11)$$

Moreover, there are general stability conditions arising from the fact that a crystal as a whole is in mechanical equilibrium: If a macroscopic crystal is rigidly translated by a vector \mathbf{u}_o , no interatomic interactions are affected and, hence, the force acting on any particular atom must vanish:

$$\sum_{\kappa' l'} V_{\alpha\beta}(\kappa l, \kappa' l') u_o^{\beta} = 0 \quad \text{for arbitrary } \mathbf{u}_o \quad (2.1.2.12)$$

and, consequently,

$$\sum_{\kappa' l'} V_{\alpha\beta}(\kappa l, \kappa' l') = 0. \quad (2.1.2.12a)$$

This relation is known as the condition of *translational invariance*.

In a similar way, it is argued that no interatomic interactions are affected when the crystal is rigidly rotated by infinitesimal amounts about arbitrary axes. This condition of *rotational invariance* leads to the following restrictions for the force constants:

$$\sum_{\kappa' l'} [V_{\alpha\beta}(\kappa l, \kappa' l') r_{\kappa' l'}^{\alpha\gamma} - V_{\alpha\gamma}(\kappa l, \kappa' l') r_{\kappa' l'}^{\alpha\beta}] = 0 \quad (2.1.2.13)$$

for all $\kappa = 1, \dots, N$ and $\alpha, \beta, \gamma = 1, 2, 3$.

In mechanical equilibrium, there must not be any strains within the crystal. The conditions of an *unstrained crystal* are also known as *Huang conditions* and may be formulated as

$$\sum_{\kappa l} \sum_{\kappa' l'} \{V_{\alpha\beta}(\kappa l, \kappa' l') [r_{\kappa l}^{\alpha\gamma} - r_{\kappa' l'}^{\alpha\gamma}] [r_{\kappa l}^{\alpha\delta} - r_{\kappa' l'}^{\alpha\delta}] - V_{\gamma\delta}(\kappa l, \kappa' l') [r_{\kappa l}^{\alpha\alpha} - r_{\kappa' l'}^{\alpha\alpha}] [r_{\kappa l}^{\alpha\beta} - r_{\kappa' l'}^{\alpha\beta}]\} = 0 \quad (2.1.2.14)$$

for all $\alpha, \beta, \gamma, \delta = 1, 2, 3$.

All these stability conditions are independent of the particular crystal structure. There are other restrictions that are due to the symmetry of the atomic arrangement. They will be considered in detail in Section 2.1.3.

2.1.2.3. The dynamical matrix

If the *ansatz* (2.1.2.10a) is inserted into the equation of motion (2.1.2.9), the following eigenvalue equation is obtained:

$$\begin{aligned} \omega_{\mathbf{q}, j}^2 \mathbf{e}_{\kappa}(\mathbf{q}, j) &= \sum_{\kappa' l'} \sqrt{\frac{1}{m_{\kappa} m_{\kappa'}}} \mathbf{V}(\kappa l, \kappa' l') \exp[i\mathbf{q}(\mathbf{r}_l - \mathbf{r}_l)] \mathbf{e}_{\kappa'}(\mathbf{q}, j) \\ &= \sum_{\kappa} \sqrt{\frac{1}{m_{\kappa} m_{\kappa'}}} \left[\sum_{l'} \mathbf{V}(\kappa l, \kappa' l') \exp[i\mathbf{q}(\mathbf{r}_l - \mathbf{r}_l)] \right] \mathbf{e}_{\kappa'}(\mathbf{q}, j). \end{aligned} \quad (2.1.2.15)$$

The summation over all primitive cells on the right-hand side of equation (2.1.2.15) yields the Fourier-transformed force-constant matrix

$$\mathbf{F}_{\kappa\kappa'}(\mathbf{q}) = \sum_{l'} \mathbf{V}(\kappa l, \kappa' l') \exp[i\mathbf{q}(\mathbf{r}_l - \mathbf{r}_l)], \quad (2.1.2.16)$$

which is independent of l for infinite crystals. $\mathbf{F}_{\kappa\kappa'}(\mathbf{q})$ contains all interactions of type κ atoms with type κ' atoms. Using this notation, equation (2.1.2.15) reduces to

$$\omega_{\mathbf{q}, j}^2 \mathbf{e}_{\kappa}(\mathbf{q}, j) = \sum_{\kappa'} \sqrt{\frac{1}{m_{\kappa} m_{\kappa'}}} \mathbf{F}_{\kappa\kappa'}(\mathbf{q}) \mathbf{e}_{\kappa'}(\mathbf{q}, j). \quad (2.1.2.17)$$

If for a given vibration characterized by (\mathbf{q}, j) we combine the three-dimensional polarization vectors $\mathbf{e}_{\kappa}(\mathbf{q}, j)$ of all atoms within a primitive cell to a $3N$ -dimensional polarization vector $\mathbf{e}(\mathbf{q}, j)$,

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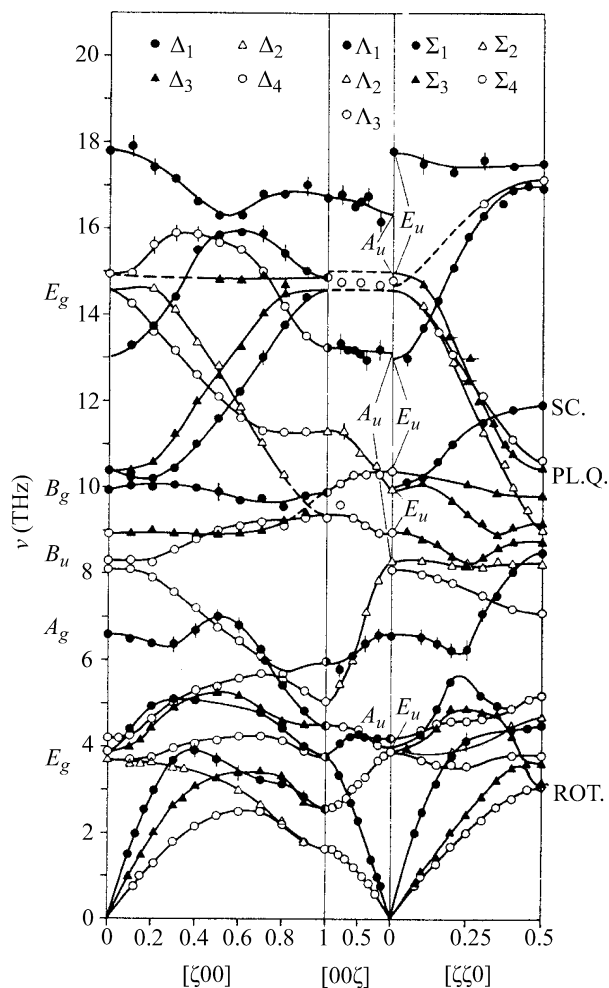


Fig. 2.1.2.4. Phonon dispersion of Nd_2CuO_4 along the main symmetry directions of the tetragonal structure. The symbols represent experimental data obtained by inelastic neutron scattering and the full lines are drawn to guide the eye. Reprinted with permission from Pintschovius *et al.* (1991), copyright (1991), with permission from Elsevier.

strongly bonded molecular groups, like SiO_4 tetrahedra in quartz or SO_4 tetrahedra in sulfates, for example, the highest frequencies are found near 35 THz and correspond to bond-stretching vibrations. Soft materials like organic molecular crystals, on the other hand, exhibit a large number of phonon branches within a rather small frequency range which cannot easily be separated. Deuterated naphthalene (C_{10}D_8) is a well investigated example. The low-frequency part of its phonon dispersion is shown in Fig. 2.1.2.5.

Whereas neutron inelastic scattering is the most powerful method for the determination of phonons at arbitrary wavevectors, long wavelength ($\mathbf{q} \rightarrow \mathbf{0}$) phonons may also be detected by optical spectroscopy. The determination of phonon frequencies alone is, however, not sufficient for a concise determination of dispersion branches. Rather, individual phonons have to be assigned uniquely to one of the $3N$ branches, and this may prove a rather hard task if N is large. Here, symmetry considerations of eigenvectors are of special importance since phonons belonging to the same branch must exhibit the same symmetry properties. Moreover, inspection of Figs. 2.1.2.3 to 2.1.2.5 shows that some of the branches cross each other and others do not. It is a general statement that crossing is only allowed for branches with different symmetries – a property which yields a classification scheme for the different phonon branches. The symmetry of fundamental vibrations of a lattice will be discussed in some detail in Section 2.1.3.

In the limit of long wavelengths, there are always three particular modes with identical polarization vectors for all atoms,

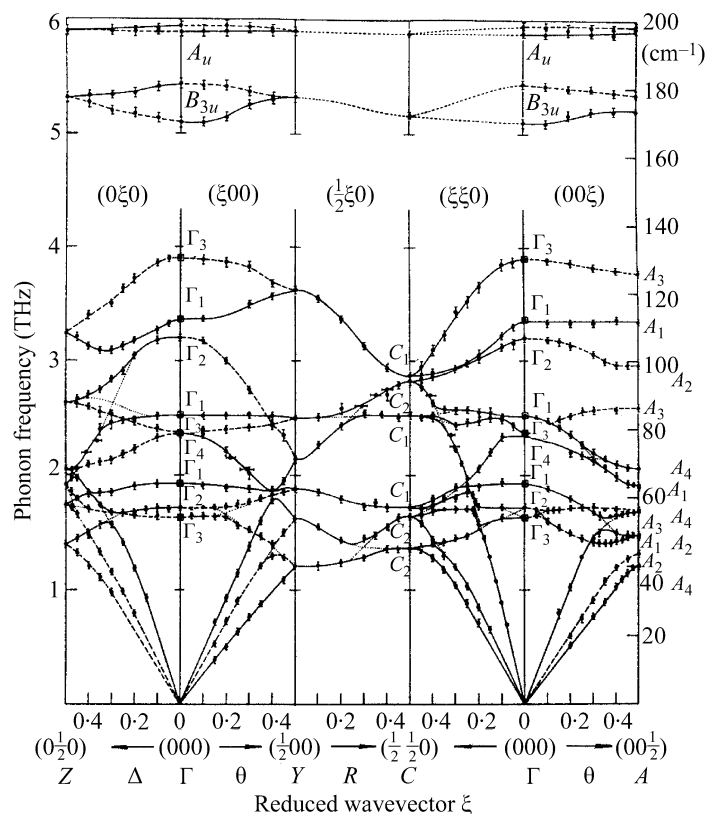


Fig. 2.1.2.5. Low-frequency part of the phonon dispersion of deuterated naphthalene at 6 K. The symbols represent experimental data obtained by inelastic neutron scattering and the full lines are drawn to guide the eye. Reproduced with permission from Natkaniec *et al.* (1980). Copyright (1980) IOP Publishing Limited.

which will be considered in the following. At exactly $\mathbf{q} = \mathbf{0}$ (the Γ point) or infinite wavelength, the eigenvalue equation (2.1.2.15) reduces to

$$\omega_{0,j}^2 \mathbf{e}_\kappa(\mathbf{0}, j) = \sum_{\kappa'l'} \frac{1}{\sqrt{m_\kappa m_{\kappa'}}} \mathbf{V}(\kappa l, \kappa' l') \mathbf{e}_{\kappa'}(\mathbf{0}, j). \quad (2.1.2.27)$$

One immediately recognizes that there are special solutions with

$$\frac{1}{\sqrt{m_\kappa}} \mathbf{e}_\kappa(\mathbf{0}, j) = \mathbf{u}_o \quad \text{for all } \kappa, \quad (2.1.2.28)$$

i.e. the (mass-weighted) eigenvectors of all atoms are identical. There are three orthogonal eigenvectors of this kind and the displacement pattern of such phonons corresponds to rigid translations of the whole lattice along the three orthogonal coordinates in direct space. These motions do not affect any interatomic interaction. Hence, there is no change in potential energy and the condition of translational invariance (*cf.* Section 2.1.2.2) guarantees that the frequencies of these modes are zero:

$$\omega_{0,j}^2 = \sum_{\kappa'l'} \mathbf{V}(\kappa l, \kappa' l') = 0 \quad \text{for } j = 1, 2, 3. \quad (2.1.2.29)$$

The phonon branches that lead to zero frequency at the Γ point ($\mathbf{q} = \mathbf{0}$) are called *acoustic*, whereas all other branches are called *optic*. The dispersion of acoustic branches in the vicinity of the Γ point can be investigated by expanding the phase factor in equation (2.1.2.15) in powers of \mathbf{q} . Using (2.1.2.28) one obtains

$$\begin{aligned} m_\kappa \omega_{\mathbf{q} \rightarrow \mathbf{0}, j}^2 \mathbf{u}_o &= \sum_{\kappa'l'} \mathbf{V}(\kappa l, \kappa' l') \{1 + i\mathbf{q}(\mathbf{r}_{l'} - \mathbf{r}_l) - \frac{1}{2}[\mathbf{q}(\mathbf{r}_{l'} - \mathbf{r}_l)]^2 + \dots\} \mathbf{u}_o. \end{aligned} \quad (2.1.2.30)$$

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Neglecting higher-order terms, summing up both sides of equation (2.1.2.30) over κ and multiplying by \mathbf{u}_o yields

$$\begin{aligned}
 M \omega_{\mathbf{q} \rightarrow 0, j}^2 \mathbf{u}_o^2 &= \sum_{\kappa} \sum_{\kappa'} \sum_{\alpha\beta} u_o^\alpha \mathbf{V}_{\alpha\beta}(\kappa l, \kappa' l') u_o^\beta \\
 &+ i \sum_{\gamma} q_{\gamma} \sum_{\kappa} \sum_{\kappa'} \sum_{\alpha\beta} u_o^\alpha V_{\alpha\beta}(\kappa l, \kappa' l') (r_l^{\alpha\gamma} - r_l'^{\alpha\gamma}) u_o^\beta \\
 &- \frac{1}{2} \sum_{\delta} \sum_{\gamma} q_{\gamma} q_{\delta} \sum_{\kappa} \sum_{\kappa'} \sum_{\alpha\beta} u_o^\alpha V_{\alpha\beta}(\kappa l, \kappa' l') \\
 &\quad \times (r_l^{\alpha\gamma} - r_l'^{\alpha\gamma}) (r_l^{\alpha\delta} - r_l'^{\alpha\delta}) u_o^\beta,
 \end{aligned} \tag{2.1.2.31}$$

M being the total mass of all atoms within the primitive cell ($M = \sum_{\kappa=1}^N m_{\kappa}$). The first term on the right-hand side is zero according to equation (2.1.2.29). The second term vanishes due to the symmetry property of the force-constant matrices, equation (2.1.2.23). Hence (2.1.2.31) is simplified to

$$\begin{aligned}
 M \left(\frac{\omega_{\mathbf{q} \rightarrow 0, j}}{|\mathbf{q}|} \right)^2 &= -\frac{1}{2} \sum_{\delta} \sum_{\gamma} \frac{q_{\gamma} q_{\delta}}{\mathbf{q}^2} \sum_{\kappa} \sum_{\kappa'} \sum_{\alpha\beta} V_{\alpha\beta}(\kappa l, \kappa' l') \\
 &\quad \times (r_l^{\alpha\gamma} - r_l'^{\alpha\gamma}) (r_l^{\alpha\delta} - r_l'^{\alpha\delta}) \frac{u_o^\alpha u_o^\beta}{\mathbf{u}_o^2}.
 \end{aligned} \tag{2.1.2.32}$$

The right-hand side no longer depends on the moduli of the wavevector and displacement but only on their orientation with respect to the crystal lattice. Consequently, acoustic dispersion curves always leave the Γ point as a straight line with a constant slope ($\omega/|\mathbf{q}|$).

The displacement pattern of these long-wavelength modes corresponds to a continuous deformation of a rigid body. Hence, acoustic phonons near the Γ point can be regarded as sound waves and the slope of the dispersion curve is given by the corresponding sound velocity,

$$v_s = \omega/|\mathbf{q}|. \tag{2.1.2.33}$$

Sound velocities, on the other hand, can be calculated from macroscopic elastic constants using the theory of macroscopic elasticity (*cf.* Chapter 1.3). Thus we are able to correlate macroscopic and microscopic dynamic properties of crystals. Using the generalized Hooke's law, the equation of motion for the dynamic deformation of a macroscopic body may be written as

$$\rho \frac{\partial^2 u_i(t)}{\partial t^2} = \sum_{k=1}^3 \sum_{l=1}^3 \sum_{m=1}^3 c_{ijklm} \frac{\partial^2 u_l}{\partial r^k \partial r^m}, \tag{2.1.2.34}$$

ρ being the macroscopic density, u_i the i th Cartesian component of the deformation and (c_{ijklm}) the symmetric tensor of elastic stiffnesses, which is discussed in detail in Chapter 1.3. The solution of this differential equation using plane waves,

$$\mathbf{u} = \mathbf{u}_o \exp[i(\mathbf{q}\mathbf{r} - \omega t)], \tag{2.1.2.35}$$

leads to the following relation:

$$\rho \left(\frac{\omega}{|\mathbf{q}|} \right)^2 u_o^j = \sum_{k=1}^3 \sum_{l=1}^3 \sum_{m=1}^3 c_{ijklm} \frac{q_k q_m}{\mathbf{q}^2} u_o^l. \tag{2.1.2.36}$$

If we define the components of the *propagation tensor* by

$$\Gamma_{jl} = \sum_{k=1}^3 \sum_{m=1}^3 c_{ijklm} \frac{q_k q_m}{\mathbf{q}^2}, \tag{2.1.2.37}$$

equation (2.1.2.36) may be written as the eigenvector equation

$$\rho v_s^2 \mathbf{u}_o = \mathbf{\Gamma} \mathbf{u}_o. \tag{2.1.2.38}$$

For a given propagation direction as defined by the Cartesian components of \mathbf{q} , the eigenvectors of the corresponding propagation tensor yield the polarization of three mutually orthogonal deformation waves. Its eigenvalues are related to the respective sound velocities $v_s = \omega/|\mathbf{q}|$. If the tensor of elastic stiffnesses is known, the elements of $\mathbf{\Gamma}$ and, hence, the velocity of elastic (sound) waves can be calculated for arbitrary propagation directions (see Section 1.3.4). These data, in turn, allow the prediction of the slopes of acoustic phonon dispersion curves near $\mathbf{q} = \mathbf{0}$.

2.1.2.5. Eigenvectors and normal coordinates

The plane-wave solutions (2.1.2.10) of the equations of motion form a complete set of orthogonal functions if \mathbf{q} is restricted to the first Brillouin zone. Hence, the actual displacement of an atom (κl) can be represented by a linear combination of the $\mathbf{u}_{\kappa l}^{\pm}(\mathbf{q}, j)$:

$$\mathbf{u}_{\kappa l} = \sum_{\mathbf{q}} \sum_j [A_{\mathbf{q}, j} \mathbf{u}_{\kappa l}^{+}(\mathbf{q}, j) + A'_{\mathbf{q}, j} \mathbf{u}_{\kappa l}^{-}(\mathbf{q}, j)]. \tag{2.1.2.39}$$

Since this displacement is an observable quantity, it must correspond to a real vector, not a complex one. Hence, the coefficients $A_{\mathbf{q}, j}$ obey the relation

$$A'_{\mathbf{q}, j} = A_{-\mathbf{q}, j}^* \tag{2.1.2.40}$$

and equation (2.1.2.39) reduces to

$$\mathbf{u}_{\kappa l} = \frac{1}{\sqrt{Nm_{\kappa}}} \sum_{\mathbf{q}} \sum_j Q_{\mathbf{q}, j} \mathbf{e}_{\kappa}(\mathbf{q}, j) \exp(i\mathbf{q}\mathbf{r}_l), \tag{2.1.2.41}$$

where

$$Q_{\mathbf{q}, j} = A_{\mathbf{q}, j} \exp(-i\omega_{\mathbf{q}, j} t) + A_{-\mathbf{q}, j}^* \exp(i\omega_{\mathbf{q}, j} t) = Q_{-\mathbf{q}, j}^*. \tag{2.1.2.42}$$

If the displacement vectors $\mathbf{u}_{\kappa l}$ are combined to form a $3N$ -dimensional vector \mathbf{u}_l in analogy to the formation of the eigenvector $\mathbf{e}(\mathbf{q}, j)$ from the individual polarization vectors $\mathbf{e}_{\kappa}(\mathbf{q}, j)$ [equation (2.1.2.18)] we obtain

$$\mathbf{u}_l = \frac{1}{\sqrt{N}} \sum_{\mathbf{q}} \sum_j Q_{\mathbf{q}, j} \mathbf{M} \mathbf{e}(\mathbf{q}, j) \exp(i\mathbf{q}\mathbf{r}_l). \tag{2.1.2.43}$$

Thus, the atomic displacement is a linear combination of the eigenvectors $\mathbf{e}(\mathbf{q}, j)$ of the dynamical matrix. The coefficients $Q_{\mathbf{q}, j}$ are called *normal coordinates*. They reflect the relative weight and amplitude of a particular vibrational mode (\mathbf{q}, j) which is temperature-dependent and may be determined by statistical methods.

In terms of these normal coordinates, the Hamiltonian of the lattice (2.1.2.8) is reduced to a sum of independent harmonic oscillators. These are called *phonons* and may be regarded as quantum quasiparticles.

$$H = \frac{N_Z}{2N} \sum_{\mathbf{q}} \sum_j \left[\left| \frac{dQ_{\mathbf{q}, j}}{dt} \right|^2 + \omega_{\mathbf{q}, j}^2 |Q_{\mathbf{q}, j}|^2 \right]. \tag{2.1.2.44}$$

(N_Z is the number of primitive cells within the crystal.)

2.1.2.6. Amplitudes of lattice vibrations

Lattice vibrations that are characterized by both the frequencies $\omega_{\mathbf{q}, j}$ and the normal coordinates $Q_{\mathbf{q}, j}$ are elementary excitations of the harmonic lattice. As long as anharmonic effects are neglected, there are no interactions between the individual phonons. The respective amplitudes depend on the excitation level and can be determined by quantum statistical methods. The energy levels of a lattice vibration (\mathbf{q}, j) are those of a single harmonic oscillator:

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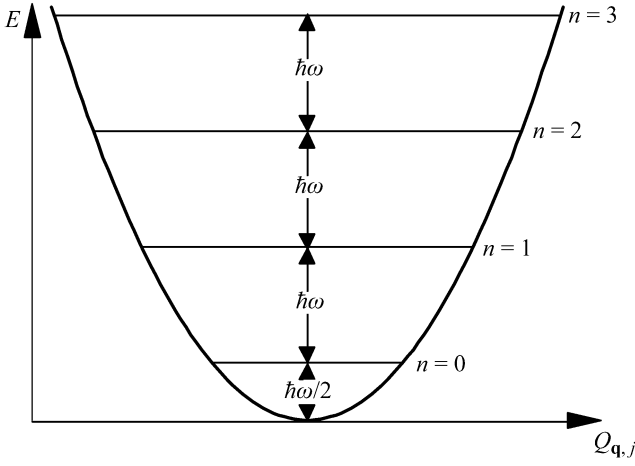


Fig. 2.1.2.6. Energy levels of a quantum-mechanical harmonic oscillator.

$$E_n = (n + \frac{1}{2})\hbar\omega_{q,j}, \quad (2.1.2.45)$$

as illustrated in Fig. 2.1.2.6. The levels are equidistant and the respective occupation probabilities are given by Boltzmann statistics:

$$P_n = \frac{\exp[-(n + 1/2)(\hbar\omega_{q,j}/kT)]}{\sum_{m=0}^{\infty} \exp[-(m + 1/2)(\hbar\omega_{q,j}/kT)]}. \quad (2.1.2.46)$$

In the quasiparticle description, this quantity is just the probability that at a temperature T there are n excited phonons of frequency $\omega_{q,j}$. Moreover, in thermal equilibrium the average number of phonons is given by the Bose factor:

$$n_{q,j} = \frac{1}{\exp(\hbar\omega_{q,j}/kT) - 1} \quad (2.1.2.47)$$

and the corresponding contribution of these phonons to the lattice energy is

$$E_{q,j} = (n_{q,j} + \frac{1}{2})\hbar\omega_{q,j}. \quad (2.1.2.48)$$

The mean-square amplitude of the normal oscillator coordinate is obtained as

$$\langle |Q_{q,j}|^2 \rangle = \frac{\hbar}{\omega_{q,j}} (n_{q,j} + \frac{1}{2}). \quad (2.1.2.49)$$

At high temperatures ($kT \gg \hbar\omega_{q,j}$), the phonon number, the corresponding energy and the amplitude approach the classical values of

$$n_{q,j} \xrightarrow{T \rightarrow \infty} \frac{kT}{\hbar\omega_{q,j}}, \quad (2.1.2.50)$$

$$E_{q,j} \xrightarrow{T \rightarrow \infty} 3NN_Z kT \quad \text{and} \quad (2.1.2.51)$$

$$\langle |Q_{q,j}|^2 \rangle \xrightarrow{T \rightarrow \infty} \frac{kT}{\omega_{q,j}^2},$$

respectively. Note that occupation number, energy and amplitude merely depend on the frequency of the particular lattice vibration. The form of the corresponding eigenvector $\mathbf{e}(\mathbf{q}, j)$ is irrelevant.

2.1.2.7. Density of states and the lattice heat capacity

The total energy stored in the harmonic phonon system is given by the sum over all phonon states (\mathbf{q}, j) :

$$E_{\text{ph}} = \sum_{\mathbf{q}} \sum_j \hbar\omega_{q,j} (n_{q,j} + \frac{1}{2}). \quad (2.1.2.52)$$

Related thermodynamic quantities like the internal energy or the heat capacity are determined by the frequency distribution of the lattice vibrations rather than by details of the phonon dispersion. Hence, it is useful to introduce the *phonon density of states* $G(\omega)$ in such a way that $G(\omega) d\omega$ is the number of phonons with frequencies between ω and $\omega + d\omega$. Using this quantity, the sum in (2.1.2.52) may be replaced by an integral expression:

$$E_{\text{ph}} - E_o = \int_0^{\infty} \frac{\hbar\omega}{\exp(\hbar\omega/kT) - 1} G(\omega) d\omega. \quad (2.1.2.53)$$

Here, E_o is the energy at $T = 0$. The derivative with respect to temperature provides the lattice heat capacity at constant volume:

$$c_V = k \int_0^{\infty} \left(\frac{\hbar\omega}{kT} \right)^2 \frac{\exp(\hbar\omega/kT)}{[\exp(\hbar\omega/kT) - 1]^2} G(\omega) d\omega. \quad (2.1.2.54)$$

As an example, Fig. 2.1.2.7 displays the phonon dispersion of GaAs as determined by inelastic neutron scattering along with the phonon density of states. Obviously, even in this relatively simple substance $G(\omega)$ (DOS) exhibits a rather complicated multi-peak structure. Integral properties like the heat capacity are, however, not very sensitive to details of $G(\omega)$. There are two well known approximations for $G(\omega)$ that are able to reproduce some prominent features of c_V :

(1) The Einstein model.

In the Einstein model, it is assumed that all phonons exhibit the same frequency ω_E (Einstein oscillator) and $G(\omega)$ is represented by a delta function:

$$G^{\text{Einstein}}(\omega) = 3NN_Z \delta(\omega - \omega_E). \quad (2.1.2.55)$$

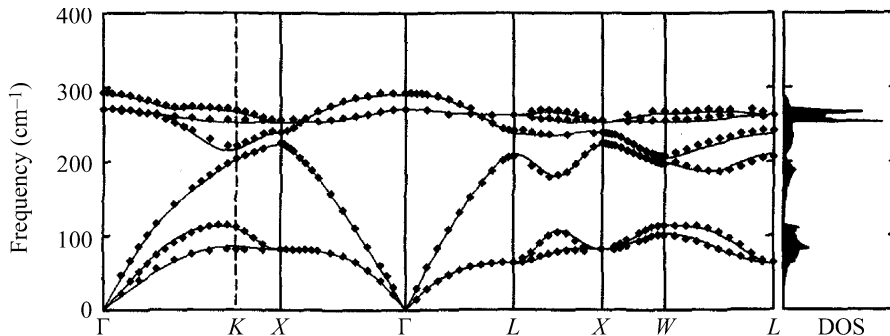


Fig. 2.1.2.7. Phonon dispersion and density of states for GaAs. The experimental data are from Strauch & Dorner (1990); the full lines and the density of states (DOS) are results of *ab initio* model calculations by Giannozzi *et al.* (1991). From Giannozzi *et al.* (1991). Copyright (1991) by the American Physical Society.

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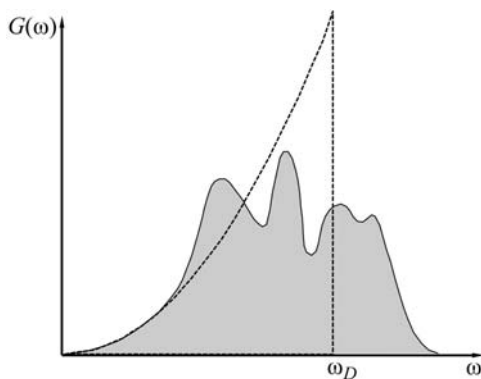


Fig. 2.1.2.8. Schematic representation of the true phonon density of states (solid line) along with the Debye approximation (dotted line). Note that the areas under the two curves are identical.

Consequently, the heat capacity turns out to be

$$c_V^{\text{Einstein}} = 3NN_Z k \left(\frac{\Theta_E}{T} \right)^2 \frac{\exp(\Theta_E/T)}{[\exp(\Theta_E/T) - 1]^2}, \quad (2.1.2.56)$$

where we use the abbreviation

$$\Theta_E = \hbar\omega_E/k, \quad (2.1.2.57)$$

which is the *Einstein temperature*.

At low temperatures, this model predicts an exponential temperature dependence of the heat capacity [$c_V \propto \exp(\Theta_E/T)$], which does not correspond to the experimental findings in most substances. Here, the *Debye model* provides a significant improvement.

(2) *The Debye model.*

In contrast to the Einstein model, which takes only one optic mode into account, the Debye model is restricted to acoustic modes that exhibit a linear dispersion close to the Γ point (see Section 2.1.2.4). Neglecting any deviation from linear behaviour, we get the simple result that the density of states is proportional to the square of the phonon frequency. The total number of phonon states is, however, given by $3NN_Z$, which is the number of all dynamical degrees of freedom of the whole system. Consequently, the frequency spectrum is assumed to be limited to frequencies below a particular value ω_D according to

$$3NN_Z = \int_0^{\omega_D} G^{\text{Debye}}(\omega) d\omega. \quad (2.1.2.58)$$

This limiting frequency is called the *Debye frequency* and is related to an appropriate average of (longitudinal and transverse) sound velocities and exhibits large values for hard materials. Fig. 2.1.2.8 compares schematically the true phonon density of states with the Debye approximation. The density of phonon states may thus be represented by

$$G^{\text{Debye}}(\omega) = 9NN_Z(\omega^2/\omega_D^3) \quad (2.1.2.59)$$

and, correspondingly, the heat capacity is

$$c_V^{\text{Debye}} = 9NN_Z k \left(\frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} \frac{x^4 \exp(x)}{[\exp(x) - 1]^2} dx, \quad (2.1.2.60)$$

yielding a temperature dependence as shown in Fig. 2.1.2.9.

Θ_D is the *Debye temperature*, which is defined as

$$\Theta_D = \hbar\omega_D/k. \quad (2.1.2.61)$$

At low temperatures, the heat capacity is proportional to T^3 , in excellent agreement with most experiments:

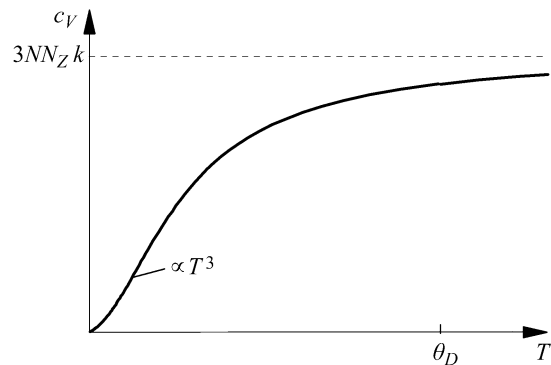


Fig. 2.1.2.9. Temperature dependence of the heat capacity at constant volume according to the Debye model.

$$c_V^{\text{Debye}} \xrightarrow{T \rightarrow 0} \frac{12}{5}\pi^4 NN_Z k (T/\Theta_D)^3. \quad (2.1.2.62)$$

It is not surprising that the Debye model provides a reasonable description of the low-temperature heat capacity, since in this temperature regime well below the Debye temperature, optical phonons are hardly excited and the heat capacity is dominated by the low-frequency acoustic modes which are modelled exactly. At higher temperatures it is, however, necessary to take into account the thermal excitation of (in general less dispersive) optic modes. This can be achieved either by introducing a temperature dependence of the Debye temperature or by mixing a Debye term like (2.1.2.60) and Einstein terms like (2.1.2.56).

As an example, we consider the case of GaAs, the density of states of which is shown in Fig. 2.1.2.7. Obviously there are two very pronounced peaks at high frequencies, which are due to nearly dispersionless optical phonon branches. These modes may therefore be regarded as Einstein oscillators. The remaining acoustic branches lead to the more continuous part of the spectrum at lower frequencies, which may be approximated by a Debye law.

2.1.2.8. Thermal expansion, compressibility and Grüneisen parameters

So far, we have always assumed that the crystal volume is constant. As long as we are dealing with harmonic solids, the thermal excitation of phonons does not result in a mean displacement of any atom. Consequently, thermal expansion cannot be understood in the harmonic approximation. It is due to the fact that there are anharmonic contributions to the lattice energy, *i.e.* third- and higher-order terms in the expansion with respect to atomic displacements [equation (2.1.2.4)]. Moreover, in an anharmonic lattice phonons are no longer independent elementary excitations. Rather, different lattice vibrations interact with each other leading to temperature-dependent frequency shifts, damping *etc.* Quantitatively, anharmonic effects may be analysed by means of perturbation theory, which is, however, beyond the scope of the present article. Details may be found, for example, in the monograph *The Physics of Phonons* (Reissland, 1973).

Some aspects of anharmonicity can, however, be discussed on the basis of the *quasi-harmonic model*. This approach makes use of the fact that the atomic interactions vary with the interatomic spacing and, hence, with the volume or, more generally, with any type of lattice deformation. The phonon frequencies will therefore depend on the deformation as well. Using the deformed lattice as a new reference frame for lattice dynamical calculations, the corresponding frequencies may be obtained again on the basis of a harmonic model with modified effective force constants. The comparison of phonons of both the original and the (arbitrarily) deformed lattice finally yields the partial derivatives of the frequencies $\omega_{\mathbf{q},j}$ with respect to the components ε_{kl} of the strain tensor.

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If the deformation is exclusively due to a change of temperature, the phonon frequency shifts can thus be related to the coefficients of thermal expansion. In this approximation, any intrinsic temperature dependence of phonon frequencies due to phonon interactions is neglected. Note that just those effects are, however, of particular importance if displacive phase transitions that are associated with soft phonon modes are considered.

In the quasi-harmonic approximation, we use the thermodynamic relation between the Helmholtz free energy A and the partition function Z :

$$A = -kT \ln Z. \quad (2.1.2.63)$$

Z is given in terms of the energy levels of the independent harmonic oscillators:

$$Z = \exp(-\Phi/kT) \prod_{\mathbf{q},j} \frac{\exp(-\hbar\omega_{\mathbf{q},j}/2kT)}{1 - \exp(-\hbar\omega_{\mathbf{q},j}/kT)}, \quad (2.1.2.64)$$

where Φ is the potential energy of the crystal if all atoms occupy their equilibrium positions. Hence, the following expression for A results:

$$A = \Phi + \frac{1}{2} \sum_{\mathbf{q},j} \hbar\omega_{\mathbf{q},j} + kT \sum_{\mathbf{q},j} \ln[1 - \exp(-\hbar\omega_{\mathbf{q},j}/kT)]. \quad (2.1.2.65)$$

Elementary thermodynamics yields the pressure p as the partial derivative of A with respect to the volume at constant temperature:

$$p = -(\partial A / \partial V)_T. \quad (2.1.2.66)$$

This relation may be generalized if not only volume changes are taken into account but also arbitrary deformations as described by the strain tensor $\boldsymbol{\varepsilon} = (\varepsilon_{kl})$:

$$\sigma_{kl} = -(1/V)(\partial A / \partial \varepsilon_{kl})_T \quad (2.1.2.67)$$

with the stress tensor $\boldsymbol{\sigma} = (\sigma_{kl})$. Note that the hydrostatic pressure p and the relative volume change are given by the traces of $\boldsymbol{\sigma}$ and $\boldsymbol{\varepsilon}$, respectively:

$$p = -\frac{1}{3} \sum_{k=1}^3 \sigma_{kk}, \quad (\Delta V/V) = \sum_{k=1}^3 \varepsilon_{kk}. \quad (2.1.2.68)$$

Taking the temperature derivative of (2.1.2.66), we obtain

$$\left(\frac{\partial \sigma_{kl}}{\partial T} \right)_{\boldsymbol{\varepsilon}} = -\frac{1}{V} \left(\frac{\partial}{\partial T} \left(\frac{\partial A}{\partial \varepsilon_{kl}} \right)_T \right)_{\boldsymbol{\varepsilon}}. \quad (2.1.2.69)$$

Using Euler's relations, the left-hand side may be written as

$$\begin{aligned} \left(\frac{\partial \sigma_{kl}}{\partial T} \right)_{\boldsymbol{\varepsilon}} &= - \sum_{mn} \left(\frac{\partial \sigma_{kl}}{\partial \varepsilon_{mn}} \right)_{T, \boldsymbol{\varepsilon}_{m'n'}} \left(\frac{\partial \varepsilon_{mn}}{\partial T} \right)_{\boldsymbol{\sigma}} \\ &= - \sum_{mn} c_{klmn} \alpha_{mn}, \end{aligned} \quad (2.1.2.70)$$

where the tensor of the elastic stiffnesses

$$c_{klmn} = \left(\frac{\partial \sigma_{kl}}{\partial \varepsilon_{mn}} \right)_{T, \boldsymbol{\varepsilon}_{m'n'}} \quad (2.1.2.71)$$

and the tensor of thermal expansion

$$\alpha_{kl} = \left(\frac{\partial \varepsilon_{kl}}{\partial T} \right)_{\boldsymbol{\sigma}} \quad (2.1.2.72)$$

have been introduced.

The free energy depends on the lattice deformations *via* the phonon frequencies. Hence, using (2.1.2.65), the right-hand side of (2.1.2.69) is evaluated as

$$\begin{aligned} \left(\frac{\partial}{\partial T} \left(\frac{\partial A}{\partial \varepsilon_{kl}} \right)_T \right)_{\boldsymbol{\varepsilon}} &= \left(\frac{\partial}{\partial T} \left(\hbar \sum_{\mathbf{q},j} \frac{1}{\exp(\hbar\omega_{\mathbf{q},j}/kT) - 1} \left(\frac{\partial \omega_{\mathbf{q},j}}{\partial \varepsilon_{kl}} \right)_T \right) \right)_{\boldsymbol{\varepsilon}} \\ &= \hbar \sum_{\mathbf{q},j} \frac{\partial n_{\mathbf{q},j}}{\partial T} \left(\frac{\partial \omega_{\mathbf{q},j}}{\partial \varepsilon_{kl}} \right)_T \end{aligned} \quad (2.1.2.73)$$

under the assumption that the phonon frequencies do not depend explicitly on the temperature. [$n_{\mathbf{q},j}$ is the Bose factor, (2.1.2.47)].

Let us denote the contribution of a single phonon (\mathbf{q}, j) to the heat capacity at constant volume by

$$\tilde{c}_{\mathbf{q},j} = \hbar\omega_{\mathbf{q},j} \frac{\partial n_{\mathbf{q},j}}{\partial T}. \quad (2.1.2.74)$$

Then the combination of (2.1.2.69), (2.1.2.70) and (2.1.2.71) yields the result

$$V \sum_{mnl} c_{klmn} \alpha_{mn} = \sum_{\mathbf{q},j} \tilde{c}_{\mathbf{q},j} \frac{\partial \ln \omega_{\mathbf{q},j}}{\partial \varepsilon_{kl}} = \sum_{\mathbf{q},j} \tilde{c}_{\mathbf{q},j} \gamma_{\mathbf{q},kl} \quad (2.1.2.75)$$

with the *generalized-mode Grüneisen parameters*

$$\gamma_{\mathbf{q},kl} = \frac{\partial \ln \omega_{\mathbf{q},j}}{\partial \varepsilon_{kl}}. \quad (2.1.2.76)$$

The set of equations (2.1.2.75) (for $k, l = 1, 2, 3$) provide relations between the variation of phonon frequencies with the lattice deformations on the one hand and the tensors of elastic stiffnesses and thermal expansion on the other hand.

For cubic crystals, the tensor of the thermal expansion is diagonal,

$$\alpha_{kl} = \frac{1}{3} \beta \delta_{kl}, \quad (2.1.2.77)$$

where β represents the coefficient of volume expansion. If Voigt's notation is used for the elastic stiffnesses (*cf.* Section 1.3.3.2.2), equation (2.1.2.75) reduces to

$$\frac{1}{3} V \beta (c_{11} + 2c_{12}) = \sum_{\mathbf{q},j} \tilde{c}_{\mathbf{q},j} \gamma_{\mathbf{q},11} = \sum_{\mathbf{q},j} \tilde{c}_{\mathbf{q},j} \gamma_{\mathbf{q},22} = \sum_{\mathbf{q},j} \tilde{c}_{\mathbf{q},j} \gamma_{\mathbf{q},33}. \quad (2.1.2.78)$$

If there is an isotropic deformation, the shift of phonon frequencies may be described by an *averaged-mode Grüneisen parameter*:

$$\gamma_{\mathbf{q},j} = \frac{1}{3} \sum_{m=1}^3 \gamma_{\mathbf{q},mm} \quad (2.1.2.79)$$

and (2.1.2.78) may be rewritten as

$$\frac{1}{3} V \beta (c_{11} + 2c_{12}) = \sum_{\mathbf{q},j} \tilde{c}_{\mathbf{q},j} \gamma_{\mathbf{q},j}. \quad (2.1.2.80)$$

Introducing the *mean Grüneisen parameter* γ by the summation over all phonon states,

$$\gamma = \frac{\sum_{\mathbf{q},j} \tilde{c}_{\mathbf{q},j} \gamma_{\mathbf{q},j}}{c_V}, \quad (2.1.2.81)$$

we arrive at

$$\frac{1}{3} V \beta (c_{11} + 2c_{12}) = \gamma c_V. \quad (2.1.2.82)$$

Remembering that in cubic crystals the expression

$$\kappa = \frac{3}{c_{11} + 2c_{12}} \quad (2.1.2.83)$$

represents the isothermal compressibility, we find the commonly used scalar form of equation (2.1.2.75):

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$$\beta = \kappa \frac{c_V \gamma}{V}, \quad (2.1.2.84)$$

which relates the thermodynamic quantities thermal expansion, compressibility and heat capacity with the mean Grüneisen parameter. For most substances, γ exhibits values between 1 and 4 which are hardly temperature dependent. Hence, equation (2.1.2.84) may be regarded as an equation of state for solid systems.

Experimentally, it is almost impossible to determine the heat capacity at constant volume c_V since the thermal expansion cannot be easily compensated. The more convenient quantity is c_p , the heat capacity at constant pressure. There is a simple thermodynamic relation between the two quantities,

$$c_p = c_V + \frac{TV\beta^2}{\kappa}, \quad (2.1.2.85)$$

and hence the following equation is obtained:

$$c_p = \left(\frac{1}{\gamma} + \beta T \right) \frac{\beta V}{\kappa}. \quad (2.1.2.86)$$

2.1.3. Symmetry of lattice vibrations

Having presented the basic formulation of lattice dynamics in Section 2.1.2, we will now consider the constraints that arise due to the symmetry of the particular atomic arrangement within a crystal. We shall see in the following how group-theoretical methods can be used in order:

(a) to reduce the number of independent elements of the dynamical matrix;

(b) to provide a unique labelling of individual phonon branches according to the symmetries of the respective eigenvectors; and

(c) to deal with degeneracies of particular phonon modes.

The theoretical aspects will be illustrated by means of simple examples which may serve as a guide for the application of the formalism to other systems of interest.

2.1.3.1. Symmetry constraints for the dynamical matrix

The elements of the $3N \times 3N$ dynamical matrix as introduced in Section 2.1.2.3 are given by

$$D_{\kappa\kappa'}^{\alpha\beta}(\mathbf{q}) = \frac{1}{\sqrt{m_\kappa m_{\kappa'}}} \sum_{l'} V_{\alpha\beta}(\kappa l, \kappa' l') \exp[i\mathbf{q}(\mathbf{r}_{l'} - \mathbf{r}_l)]. \quad (2.1.3.1)$$

Using the matrix notation for the 3×3 submatrices introduced in (2.1.2.22a), this equation reads

$$\mathbf{D}_{\kappa\kappa'}(\mathbf{q}) = \frac{1}{\sqrt{m_\kappa m_{\kappa'}}} \sum_{l'} \mathbf{V}(\kappa l, \kappa' l') \exp[i\mathbf{q}(\mathbf{r}_{l'} - \mathbf{r}_l)]. \quad (2.1.3.1a)$$

Since the vector $\mathbf{r}_{l'} - \mathbf{r}_l$ corresponds to a vector of the direct lattice, the right-hand side of equation (2.1.3.1) is invariant with respect to changes of the wavevector \mathbf{q} by an arbitrary reciprocal lattice vector \mathbf{g} . Hence, the elements of the dynamical matrix represent periodic functions within the reciprocal space:

$$\mathbf{D}(\mathbf{q} + \mathbf{g}) = \mathbf{D}(\mathbf{q}). \quad (2.1.3.2)$$

² If for a given wavevector \mathbf{q} the dynamical matrix exhibits degenerate eigenvalues, the most one can strictly infer from equation (2.1.3.2) is that the eigenvector $\mathbf{e}(\mathbf{q} + \mathbf{g}, j)$ may be represented by some linear combination of those eigenvectors $\mathbf{e}(\mathbf{q}, j')$ that correspond to the same eigenvalue. One always can choose, however, an appropriate labelling of the degenerate phonon modes and appropriate phase factors for the eigenvectors in order to guarantee that the simple relation (2.1.3.3) holds.

The same periodicity can also be assumed for the eigenvalues, or eigenfrequencies, and for the eigenvectors:²

$$\begin{aligned} \omega_{\mathbf{q}+\mathbf{g},j} &= \omega_{\mathbf{q},j}, \\ \mathbf{e}(\mathbf{q} + \mathbf{g}, j) &= \mathbf{e}(\mathbf{q}, j). \end{aligned} \quad (2.1.3.3)$$

Consequently, we can restrict our discussion to wavevectors within the first Brillouin zone.

Owing to the symmetry of the atomic structure, not all of the force constants $V_{\alpha\beta}(\kappa l, \kappa' l')$ reflecting the interaction between atoms (κl) and ($\kappa' l'$) are independent. Rather, there are constraints to the elements of the dynamical matrix according to the space group of the crystal. In the following, these constraints will be considered in some detail. Suppose the space group contains a symmetry operation $\{\mathbf{S}|\mathbf{v}(\mathbf{S}) + \mathbf{x}(m)\}$.³ When applied to the crystal, this symmetry operation sends atom (κl) into another atom (KL) and simultaneously atom ($\kappa' l'$) into ($K'L'$). At the same time, the wavevector of a phonon is rotated from \mathbf{q} into $\mathbf{S}\mathbf{q}$. Hence, the elements of the dynamical matrix that describes the dynamics of the crystal after application of the symmetry operation may be written as

$$\begin{aligned} D_{KK'}^{\alpha\beta}(\mathbf{S}\mathbf{q}) &= \frac{1}{\sqrt{m_K m_{K'}}} \sum_{L'} V_{\alpha\beta}(KL, K'L') \exp[i(\mathbf{S}\mathbf{q})(\mathbf{r}_{L'} - \mathbf{r}_L)] \end{aligned} \quad (2.1.3.4)$$

or in submatrix notation

$$\mathbf{D}_{KK'}(\mathbf{S}\mathbf{q}) = \frac{1}{\sqrt{m_K m_{K'}}} \sum_{L'} \mathbf{V}(KL, K'L') \exp[i(\mathbf{S}\mathbf{q})(\mathbf{r}_{L'} - \mathbf{r}_L)]. \quad (2.1.3.4a)$$

This submatrix can be related to the corresponding matrix $\mathbf{D}_{\kappa\kappa'}(\mathbf{q})$ that describes the same dynamical behaviour, but in the unrotated crystal. To this end, we first consider the transformation of the force-constant matrices under the symmetry operation. Obviously, the interaction between atoms (κl) and ($\kappa' l'$) has to be of the same type as the interaction between (KL) and ($K'L'$).

Since the potential energy is invariant with respect to symmetry operations, the force constants are related *via*

$$\begin{aligned} \sum_{\alpha\beta} \sum_{\kappa l} \sum_{\kappa' l'} V_{\alpha\beta}(\kappa l, \kappa' l') u_{\kappa l}^\alpha u_{\kappa' l'}^\beta &= \sum_{\alpha\beta} \sum_{KL} \sum_{K'L'} V_{\alpha\beta}(KL, K'L') u_{KL}^\alpha u_{K'L'}^\beta \end{aligned} \quad (2.1.3.5)$$

or in matrix notation

$$\sum_{\kappa l} \sum_{\kappa' l'} \mathbf{u}_{\kappa l} \mathbf{V}(\kappa l, \kappa' l') \mathbf{u}_{\kappa' l'} = \sum_{KL} \sum_{K'L'} \mathbf{u}_{KL} \mathbf{V}(KL, K'L') \mathbf{u}_{K'L'}. \quad (2.1.3.5a)$$

Owing to the symmetry operation, the displacements of atoms (κl) and ($\kappa' l'$) are rotated and transferred to atoms (KL) and ($K'L'$), respectively (see Fig. 2.1.3.1). Thus, (2.1.3.5) can be rewritten as

$$\begin{aligned} \sum_{\alpha\beta} \sum_{\kappa l} \sum_{\kappa' l'} V_{\alpha\beta}(\kappa l, \kappa' l') u_\alpha(\kappa l) u_\beta(\kappa' l') &= \sum_{\alpha\beta} \sum_{\kappa l} \sum_{\kappa' l'} V_{\alpha\beta}(KL, K'L') \sum_{\mu} S_{\alpha\mu} u_\mu(\kappa l) \sum_{\nu} S_{\beta\nu} u_\nu(\kappa' l'). \end{aligned} \quad (2.1.3.6)$$

³ We use the Seitz notation for symmetry operations: \mathbf{S} denotes a rigid rotation of the lattice, $\mathbf{v}(\mathbf{S})$ is the corresponding vector of a fractional translation in the case of screw axes, glide planes *etc.* and $\mathbf{x}(m)$ is a lattice vector.

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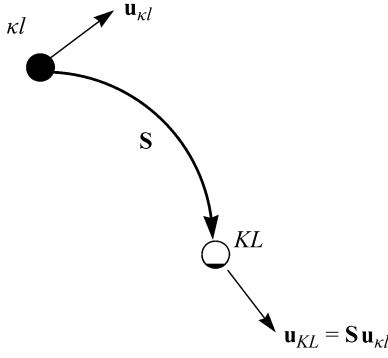


Fig. 2.1.3.1. Transformation of atomic displacements by a symmetry operation.

Moreover, this relation is valid for arbitrary displacements and, hence, the matrices of force constants transform according to

$$V_{\mu\nu}(\kappa l, \kappa' l') = \sum_{\alpha\beta} V_{\alpha\beta}(KL, K'L') S_{\alpha\mu} S_{\beta\nu} \quad (2.1.3.7)$$

or

$$\mathbf{V}(\kappa l, \kappa' l') = \mathbf{S}^T \mathbf{V}(KL, K'L') \mathbf{S}. \quad (2.1.3.7a)$$

Using the fact that the matrix of rotation \mathbf{S} is unitary ($\mathbf{S}^{-1} = \mathbf{S}^T$), the inverse relation is obtained:

$$\mathbf{V}(KL, K'L') = \mathbf{S} \mathbf{V}(\kappa l, \kappa' l') \mathbf{S}^T. \quad (2.1.3.7b)$$

Hence, the force-constant submatrices transform like tensors do. One has to bear in mind, however, that the matrices in equation (2.1.3.7b) correspond to different pairs of atoms as illustrated by Fig. 2.1.3.2. Using this result in equation (2.1.3.4a) and remembering the fact that atoms related by a symmetry operation have the same mass, we obtain

$$\begin{aligned} D_{KK'}^{\alpha\beta}(\mathbf{S}\mathbf{q}) &= \frac{1}{\sqrt{m_\kappa m_{\kappa'}}} \sum_{\mu\nu} S_{\alpha\mu} S_{\beta\nu} \sum_{l'} V_{\mu\nu}(\kappa l, \kappa' l') \exp[i(\mathbf{S}\mathbf{q})(\mathbf{r}_{L'} - \mathbf{r}_L)] \\ &= \frac{1}{\sqrt{m_\kappa m_{\kappa'}}} \sum_{\mu\nu} S_{\alpha\mu} S_{\beta\nu} \sum_{l'} V_{\mu\nu}(\kappa l, \kappa' l') \exp[i\mathbf{q} \mathbf{S}^{-1}(\mathbf{r}_{L'} - \mathbf{r}_L)]. \end{aligned} \quad (2.1.3.8)$$

The phase factor on the right-hand side contains the indices L and L' of those primitive cells into which the atoms (κl) and ($\kappa' l'$) are sent by the symmetry operation $\{\mathbf{S}|\mathbf{v}(\mathbf{S}) + \mathbf{x}(m)\}$. In general, the phase is not conserved during the transformation and, hence, the sum over l' cannot simply be replaced by the matrix elements $D_{\kappa\kappa'}^{\mu\nu}(\mathbf{q})$. Rather, we have to consider the phase factor in more detail in order to find the transformation law for the dynamical matrix.

The position vectors of particles (κl) and (KL) are related via

$$\begin{aligned} \mathbf{r}_{KL}^o &= \mathbf{r}_K^o + \mathbf{r}_L = \{\mathbf{S}|\mathbf{v}(\mathbf{S}) + \mathbf{x}(m)\} \mathbf{r}_{\kappa l}^o \\ &= \mathbf{S} \mathbf{r}_{\kappa l}^o + \mathbf{v}(\mathbf{S}) + \mathbf{x}(m) \\ &= \mathbf{S}(\mathbf{r}_\kappa^o + \mathbf{r}_l) + \mathbf{v}(\mathbf{S}) + \mathbf{x}(m) \end{aligned} \quad (2.1.3.9)$$

and

$$\begin{aligned} \mathbf{r}_\kappa^o + \mathbf{r}_l &= \mathbf{S}^{-1}(\mathbf{r}_K^o + \mathbf{r}_L) - \mathbf{v}(\mathbf{S}) - \mathbf{x}(m) \\ &= \{\mathbf{S}|\mathbf{v}(\mathbf{S}) + \mathbf{x}(m)\}^{-1} \mathbf{r}_K^o + \mathbf{S}^{-1} \mathbf{r}_L. \end{aligned} \quad (2.1.3.9a)$$

Consequently, the vector appearing in the phase factor of equation (2.1.3.8) can be expressed as

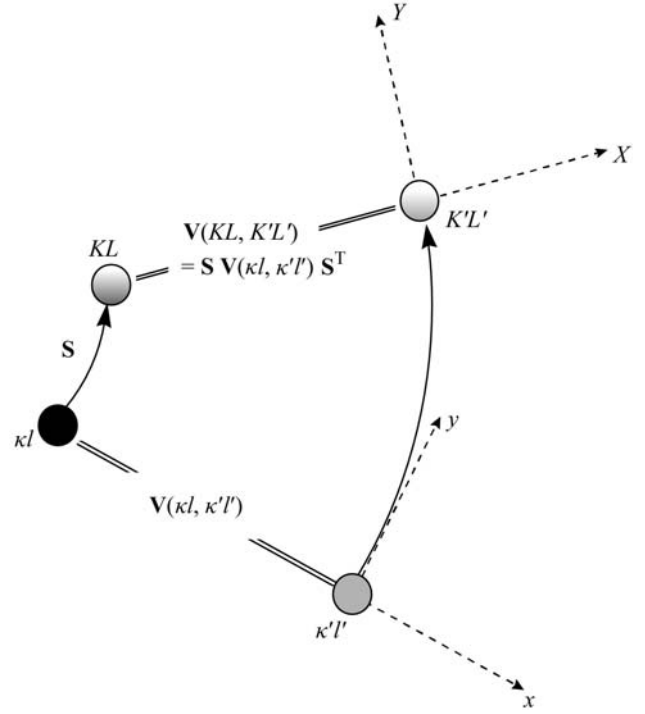


Fig. 2.1.3.2. Relation between interaction of symmetry-related atoms.

$$\mathbf{S}^{-1} \mathbf{r}_L = \mathbf{r}_\kappa^o + \mathbf{r}_l - \{\mathbf{S}|\mathbf{v}(\mathbf{S}) + \mathbf{x}(m)\}^{-1} \mathbf{r}_K^o. \quad (2.1.3.10)$$

When inserted into equation (2.1.3.8), the required transformation law for the dynamical matrix is obtained:

$$\begin{aligned} D_{KK'}^{\alpha\beta}(\mathbf{S}\mathbf{q}) &= \frac{1}{\sqrt{m_\kappa m_{\kappa'}}} \sum_{\mu\nu} S_{\alpha\mu} S_{\beta\nu} \sum_{l'} V_{\mu\nu}(\kappa l, \kappa' l') \\ &\quad \times \exp[i\mathbf{q}(\mathbf{r}_{l'} - \mathbf{r}_l)] \\ &\quad \times \exp[i\mathbf{q}(\{\mathbf{S}|\mathbf{v}(\mathbf{S}) + \mathbf{x}(m)\}^{-1} \mathbf{r}_K^o - \mathbf{r}_\kappa^o)] \\ &\quad \times \exp[-i\mathbf{q}(\{\mathbf{S}|\mathbf{v}(\mathbf{S}) + \mathbf{x}(m)\}^{-1} \mathbf{r}_{K'}^o - \mathbf{r}_{\kappa'}^o)] \end{aligned} \quad (2.1.3.11)$$

or

$$\begin{aligned} D_{KK'}^{\alpha\beta}(\mathbf{S}\mathbf{q}) &= \sum_{\mu\nu} S_{\alpha\mu} S_{\beta\nu} D_{\kappa\kappa'}^{\mu\nu}(\mathbf{q}) \\ &\quad \times \exp[i\mathbf{q}(\{\mathbf{S}|\mathbf{v}(\mathbf{S}) + \mathbf{x}(m)\}^{-1} \mathbf{r}_K^o - \mathbf{r}_\kappa^o)] \\ &\quad \times \exp[-i\mathbf{q}(\{\mathbf{S}|\mathbf{v}(\mathbf{S}) + \mathbf{x}(m)\}^{-1} \mathbf{r}_{K'}^o - \mathbf{r}_{\kappa'}^o)], \end{aligned} \quad (2.1.3.11a)$$

or in submatrix notation

$$\begin{aligned} \mathbf{D}_{KK'}(\mathbf{S}\mathbf{q}) &= \mathbf{S}^T \mathbf{D}_{\kappa\kappa'}(\mathbf{q}) \mathbf{S} \\ &\quad \times \exp[i\mathbf{q}(\{\mathbf{S}|\mathbf{v}(\mathbf{S}) + \mathbf{x}(m)\}^{-1} \mathbf{r}_K^o - \mathbf{r}_\kappa^o)] \\ &\quad \times \exp[-i\mathbf{q}(\{\mathbf{S}|\mathbf{v}(\mathbf{S}) + \mathbf{x}(m)\}^{-1} \mathbf{r}_{K'}^o - \mathbf{r}_{\kappa'}^o)]. \end{aligned} \quad (2.1.3.11b)$$

Again, these are relations between pairs of submatrices of the dynamical matrix. In contrast to the matrices of force constants, however, phase factors have to be considered here. This is because the symmetry operation $\{\mathbf{S}|\mathbf{v}(\mathbf{S}) + \mathbf{x}(m)\}$ may send different atoms κ and κ' located within the same primitive cell (0) into atoms (KL) and ($K'L'$) within different primitive cells L and L' as illustrated in Fig. 2.1.3.3. Therefore, the product of phase factors in equation (2.1.3.11) is in general different from unity.

Irrespective of the particular primitive cells in which the atoms are located, however, the labels κ and K of those atoms that are related by a symmetry operation are uniquely determined. Given

2. SYMMETRY ASPECTS OF EXCITATIONS

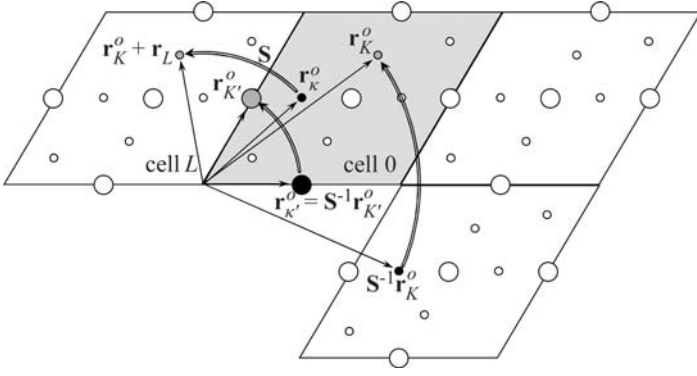


Fig. 2.1.3.3. Symmetry-related atoms in different primitive cells.

the label κ and a particular symmetry operation $\{\mathbf{S}|\mathbf{v}(\mathbf{S}) + \mathbf{x}(m)\}$, the label K may be represented by the function

$$K = F_o(\kappa, \mathbf{S}), \quad (2.1.3.12)$$

which represents the atom transformation table.⁴ With the definition of unitary transformation matrices

$$\begin{aligned} \Gamma_{K\kappa}^{\alpha\mu}(\mathbf{q}, \{\mathbf{S}|\mathbf{v}(\mathbf{S}) + \mathbf{x}(m)\}) \\ = S_{\alpha\mu} \delta(\kappa, F_o^{-1}(K, \mathbf{S})) \exp[i\mathbf{q} (\{\mathbf{S}|\mathbf{v}(\mathbf{S}) + \mathbf{x}(m)\}^{-1} \mathbf{r}_K^o - \mathbf{r}_\kappa^o)], \end{aligned} \quad (2.1.3.13)$$

we are now able to formulate the transformation law for the dynamical matrix briefly as

$$\begin{aligned} \mathbf{D}(\mathbf{S} \mathbf{q}) \\ = \mathbf{\Gamma}(\mathbf{q}, \{\mathbf{S}|\mathbf{v}(\mathbf{S}) + \mathbf{x}(m)\}) \mathbf{D}(\mathbf{q}) \mathbf{\Gamma}^+(\mathbf{q}, \{\mathbf{S}|\mathbf{v}(\mathbf{S}) + \mathbf{x}(m)\}). \end{aligned} \quad (2.1.3.14)$$

Obviously, with the help of equation (2.1.3.13), we can allocate a unitary matrix to each symmetry operation. These $\mathbf{\Gamma}$ matrices, however, do not form a representation of the crystal space group in the mathematical sense since the mapping

$$\{\mathbf{S}|\mathbf{v}(\mathbf{S}) + \mathbf{x}(m)\} \rightarrow \mathbf{\Gamma}(\mathbf{q}, \{\mathbf{S}|\mathbf{v}(\mathbf{S}) + \mathbf{x}(m)\})$$

is not a linear one. Rather, we obtain the following transformation matrix for the product of two symmetry operations:

$$\begin{aligned} \mathbf{\Gamma}(\mathbf{q}, \{\mathbf{S}_1|\mathbf{v}(\mathbf{S}_1) + \mathbf{x}(m_1)\} \circ \{\mathbf{S}_2|\mathbf{v}(\mathbf{S}_2) + \mathbf{x}(m_2)\}) \\ = \mathbf{\Gamma}(\mathbf{S}_2 \mathbf{q}, \{\mathbf{S}_1|\mathbf{v}(\mathbf{S}_1) + \mathbf{x}(m_1)\}) \mathbf{\Gamma}(\mathbf{q}, \{\mathbf{S}_2|\mathbf{v}(\mathbf{S}_2) + \mathbf{x}(m_2)\}). \end{aligned} \quad (2.1.3.15)$$

The nonlinearity of the mapping is due to the fact that the first matrix on the right-hand side of this equation depends on the wavevector $\mathbf{S}_2 \mathbf{q}$ rather than on \mathbf{q} . If we restrict our considerations to the symmetry operations of the *space group* $G(\mathbf{q})$ of the wavevector \mathbf{q} that leave the wavevector invariant modulo some reciprocal-lattice vector $\mathbf{g}(\mathbf{q}, \mathbf{S})$,

$$\mathbf{S} \mathbf{q} = \mathbf{q} - \mathbf{g}(\mathbf{q}, \mathbf{S}), \quad (2.1.3.16)$$

then equation (2.1.3.13) provides an ordinary ($3N$ -dimensional) representation of this symmetry group.⁵ In the following, we denote the elements of the subgroup $G(\mathbf{q})$ by $\{\mathbf{R}|\mathbf{v}(\mathbf{R}) + \mathbf{x}(m)\}$.

⁴ Since the rotation \mathbf{S} uniquely defines the fractional translation $\mathbf{v}(\mathbf{S})$ and since a lattice translation $\mathbf{x}(m)$ never changes the label of an atom within the primitive cell, the function F_o depends only on \mathbf{S} .

⁵ According to (2.1.3.10), the vector $\{\mathbf{S}|\mathbf{v}(\mathbf{S}) + \mathbf{x}(m)\}^{-1} \mathbf{r}_K^o - \mathbf{r}_\kappa^o$ is always a lattice vector. Hence, the transformation matrix remains invariant when the wavevector is shifted by a reciprocal-lattice vector. If wavevectors within the first Brillouin zone are considered, $\mathbf{g}(\mathbf{q}, \mathbf{S})$ is always zero. For wavevectors on the Brillouin-zone boundary, however, there may be symmetry operations like the inversion that transform \mathbf{q} into another equivalent but not identical vector $\mathbf{q}' = \mathbf{q} + \mathbf{g}$.

The corresponding unitary and Hermitian transformation matrices can be reduced to

$$\begin{aligned} \Gamma_{K\kappa}^{\alpha\mu}(\mathbf{q}, \{\mathbf{R}|\mathbf{v}(\mathbf{R}) + \mathbf{x}(m)\}) \\ = R_{\alpha\mu} \delta(\kappa, F_o^{-1}(K; \mathbf{R})) \\ \times \exp[i\mathbf{q} (\mathbf{R}^{-1} \mathbf{r}_K^o - \mathbf{R}^{-1} \mathbf{v}(\mathbf{R}) - \mathbf{R}^{-1} \mathbf{x}(m) - \mathbf{r}_\kappa^o)] \\ = R_{\alpha\mu} \delta(\kappa, F_o^{-1}(K; \mathbf{R})) \\ \times \exp[i\mathbf{R} \mathbf{q} (\mathbf{r}_K^o - \{\mathbf{R}|\mathbf{v}(\mathbf{R}) + \mathbf{x}(m)\} \mathbf{r}_\kappa^o)] \\ = R_{\alpha\mu} \delta(\kappa, F_o^{-1}(K; \mathbf{R})) \\ \times \exp[i\mathbf{q} (\mathbf{r}_K^o - \{\mathbf{R}|\mathbf{v}(\mathbf{R}) + \mathbf{x}(m)\} \mathbf{r}_\kappa^o)]. \end{aligned} \quad (2.1.3.17)$$

According to equation (2.1.3.14), they commute with the dynamical matrix:

$$\mathbf{\Gamma}(\mathbf{q}, \{\mathbf{R}|\mathbf{v}(\mathbf{R}) + \mathbf{x}(m)\}) \mathbf{D}(\mathbf{q}) \mathbf{\Gamma}^{-1}(\mathbf{q}, \{\mathbf{R}|\mathbf{v}(\mathbf{R}) + \mathbf{x}(m)\}) = \mathbf{D}(\mathbf{q}). \quad (2.1.3.18)$$

This relation contains the symmetry constraints for the dynamical matrix. The independent elements of $\mathbf{D}(\mathbf{q})$ may be obtained by application of equation (2.1.3.18) for every operation of the space group of the wavevector.

Another approach to the symmetry reduction of the dynamical matrix is based on group-theoretical considerations making use of the well known irreducible representations of symmetry groups. It is especially useful for the prediction of the form of eigenvectors and the investigation of degeneracies. Following the treatment of Maradudin & Vosko (1968), we consider the purely rotational elements of the space group $G(\mathbf{q})$ that form the *point group of the wavevector* $G_o(\mathbf{q}) = \{\mathbf{R}\}$. According to equation (2.1.3.17), we associate a matrix operator

$$\mathbf{T}(\mathbf{q}, \mathbf{R}) = \exp[i\mathbf{q} (\mathbf{v}(\mathbf{R}) + \mathbf{x}(m))] \mathbf{\Gamma}(\mathbf{q}, \{\mathbf{R}|\mathbf{v}(\mathbf{R}) + \mathbf{x}(m)\}) \quad (2.1.3.19)$$

to each of the elements of $G_o(\mathbf{q})$. These matrix operators are uniquely determined by the rotations \mathbf{R} and do not depend on the translational parts of the space-group operation $\{\mathbf{R}|\mathbf{v}(\mathbf{R}) + \mathbf{x}(m)\}$, as proven by inspection of the individual matrix elements:

$$T_{K\kappa}^{\alpha\mu}(\mathbf{q}, \mathbf{R}) = R_{\alpha\mu} \delta(\kappa, F_o^{-1}(K, \mathbf{R})) \exp[i\mathbf{q} (\mathbf{r}_K^o - \mathbf{R} \mathbf{r}_\kappa^o)]. \quad (2.1.3.19a)$$

These \mathbf{T} matrices again commute with the dynamical matrix,

$$\mathbf{T}(\mathbf{q}, \mathbf{R}) \mathbf{D}(\mathbf{q}) \mathbf{T}^{-1}(\mathbf{q}, \mathbf{R}) = \mathbf{D}(\mathbf{q}), \quad (2.1.3.20)$$

but in contrast to the $\mathbf{\Gamma}$ matrices they do not provide an ordinary representation of the group $G_o(\mathbf{q})$. For the multiplication of two symmetry elements \mathbf{R}_i and \mathbf{R}_j the following relation holds:

$$\begin{aligned} \mathbf{T}(\mathbf{q}, \mathbf{R}_i) \mathbf{T}(\mathbf{q}, \mathbf{R}_j) \\ = \exp[i(\mathbf{q} - \mathbf{R}_i^{-1} \mathbf{q})(\mathbf{v}(\mathbf{R}_j) + \mathbf{x}(m_j))] \mathbf{T}(\mathbf{q}, \mathbf{R}_i \circ \mathbf{R}_j). \end{aligned} \quad (2.1.3.21)$$

According to equation (2.1.3.16), $\mathbf{q} - \mathbf{R}_i^{-1} \mathbf{q}$ is a reciprocal-lattice vector $\mathbf{g}(\mathbf{q}, \mathbf{R}_i^{-1})$ and hence

$$\begin{aligned} \mathbf{T}(\mathbf{q}, \mathbf{R}_i) \mathbf{T}(\mathbf{q}, \mathbf{R}_j) = \exp[i\mathbf{g}(\mathbf{q}, \mathbf{R}_i^{-1}) \mathbf{v}(\mathbf{R}_j)] \mathbf{T}(\mathbf{q}, \mathbf{R}_i \circ \mathbf{R}_j) \\ = \varphi(\mathbf{q}, \mathbf{R}_i, \mathbf{R}_j) \mathbf{T}(\mathbf{q}, \mathbf{R}_i \circ \mathbf{R}_j). \end{aligned} \quad (2.1.3.21a)$$

Thus, the \mathbf{T} matrices provide not a normal but a *multiplier representation* of the group $G_o(\mathbf{q})$. The phase factor on the right-hand side of equation (2.1.3.21a) is the complex multiplier characteristic for the (ordered) product of symmetry operations.

2.1. PHONONS

For wavevectors within the first Brillouin zone, the reciprocal-lattice vectors $\mathbf{g}(\mathbf{q}, \mathbf{R}_i^{-1})$ are identically zero (see last footnote) and the \mathbf{T} representation is an ordinary one. The same is true if none of the symmetry elements of $G_o(\mathbf{q})$ contains a fractional translation, *i.e.* for symmorphic space groups. Therefore, multipliers have to be taken into account only if nonsymmorphic space groups and wavevectors on the Brillouin-zone boundary are considered.

There are some other restrictions for the dynamical matrix arising from the fact that inverting the wavevector is equivalent to taking the complex conjugate dynamical matrix [*c.f.* equation (2.1.2.24)]:

$$\mathbf{D}^*(\mathbf{q}) = \mathbf{D}(-\mathbf{q}). \quad (2.1.3.22)$$

Hence it is useful to extend our discussion to those symmetry operations that invert the phonon wavevector. Let us assume that the space group of the crystal contains an element $\{\mathbf{S}_-|\mathbf{v}(\mathbf{S}_-)\}$ with

$$\mathbf{S}_- \mathbf{q} = -\mathbf{q}. \quad (2.1.3.23)$$

Using equation (2.1.3.14) we obtain

$$\mathbf{D}(-\mathbf{q}) = \mathbf{D}^*(\mathbf{q}) = \Gamma(\mathbf{q}, \{\mathbf{S}_-|\mathbf{v}(\mathbf{S}_-)\}) \mathbf{D}(\mathbf{q}) \Gamma^+(\mathbf{q}, \{\mathbf{S}_-|\mathbf{v}(\mathbf{S}_-)\}). \quad (2.1.3.24)$$

In order to provide a consistent description, we introduce an anti-unitary operator \mathbf{K}_o which transforms an arbitrary vector Ψ into its complex conjugate counterpart Ψ^*

$$\mathbf{K}_o \Psi = \Psi^*. \quad (2.1.3.25)$$

Obviously, \mathbf{K}_o does not commute with the dynamical matrix but exhibits the following transformation behaviour:

$$\mathbf{K}_o \mathbf{D}(\mathbf{q}) \mathbf{K}_o = \mathbf{D}^*(\mathbf{q}). \quad (2.1.3.26)$$

On the other hand, we infer from equation (2.1.3.24) that

$$\begin{aligned} & \mathbf{K}_o \Gamma(\mathbf{q}, \{\mathbf{S}_-|\mathbf{v}(\mathbf{S}_-)\}) \mathbf{D}(\mathbf{q}) \Gamma^+(\mathbf{q}, \{\mathbf{S}_-|\mathbf{v}(\mathbf{S}_-)\}) \mathbf{K}_o \\ &= \mathbf{K}_o \mathbf{D}(-\mathbf{q}) \mathbf{K}_o \\ &= \mathbf{D}^*(-\mathbf{q}) \\ &= \mathbf{D}(\mathbf{q}), \end{aligned} \quad (2.1.3.27)$$

which provide the additional constraints for the dynamical matrix. In component form, this last relation can be written explicitly as

$$\begin{aligned} & [\exp(-i\mathbf{q}\mathbf{r}_K) D_{KK'}^{\mu\nu}(\mathbf{q}) \exp(i\mathbf{q}\mathbf{r}_{K'})]^* \\ &= \sum_{\alpha\beta} (S_-)_{\mu\alpha} [\exp(-i\mathbf{q}\mathbf{r}_K) D_{KK'}^{\alpha\beta}(\mathbf{q}) \exp(i\mathbf{q}\mathbf{r}_{K'})] (S_-)_{\nu\beta} \end{aligned} \quad (2.1.3.28)$$

if particles (κl) and ($\kappa' l'$) are sent into (KL) and ($K'L'$) by the symmetry operation $\{\mathbf{S}_-|\mathbf{v}(\mathbf{S}_-)\}$, respectively.

If \mathbf{S}_- represents the inversion $((S_-)_{\alpha\beta} = -\delta_{\alpha\beta})$, in particular, then (2.1.3.28) reduces to

$$[\exp(-i\mathbf{q}\mathbf{r}_K) D_{KK'}^{\mu\nu}(\mathbf{q}) \exp(i\mathbf{q}\mathbf{r}_{K'})]^* = [\exp(-i\mathbf{q}\mathbf{r}_K) D_{KK'}^{\mu\nu}(\mathbf{q}) \exp(i\mathbf{q}\mathbf{r}_{K'})]. \quad (2.1.3.29)$$

Moreover, if every atom is itself a centre of inversion (*e.g.* the NaCl structure) ($K = \kappa$ and $K' = \kappa'$), the matrix $\mathbf{C}(\mathbf{q})$ defined by

$$C_{\kappa\kappa'}^{\alpha\beta}(\mathbf{q}) = \exp(-i\mathbf{q}\mathbf{r}_\kappa) D_{\kappa\kappa'}^{\alpha\beta}(\mathbf{q}) \exp(i\mathbf{q}\mathbf{r}_{\kappa'}) \quad (2.1.3.30)$$

is a real and symmetric matrix with real eigenvectors for arbitrary wavevectors \mathbf{q} .

In terms of group theory we proceed as follows: We add to the space group of the wavevector $G(\mathbf{q})$ the elements of the coset $\{\mathbf{S}_-|\mathbf{v}(\mathbf{S}_-)\} \circ G(\mathbf{q})$.⁶ This will result in a new space group which we call $G(\mathbf{q}, -\mathbf{q})$. If instead of the matrix operator $\Gamma(\mathbf{q}, \{\mathbf{S}|\mathbf{v}(\mathbf{S}) + \mathbf{x}(m)\})$ the anti-unitary operator $\mathbf{K}_o \Gamma(\mathbf{q}, \{\mathbf{S}_-|\mathbf{v}(\mathbf{S}_-) + \mathbf{x}(m)\})$ is assigned to those symmetry operations that invert the wavevector, then a representation of the whole group $G(\mathbf{q}, -\mathbf{q})$ is provided. Moreover, all these matrix operators commute with the dynamical matrix.

As before, let us restrict ourselves to the rotational parts of the symmetry operations. The point group of the wavevector $G_o(\mathbf{q})$ is enlarged by the coset $\mathbf{S}_- \circ G_o(\mathbf{q})$ yielding the group $G_o(\mathbf{q}, -\mathbf{q})$. In analogy to equation (2.1.3.19), the elements of the left coset will be represented by the matrix operator

$$\begin{aligned} \mathbf{T}(\mathbf{q}, \mathbf{S}_- \circ \mathbf{R}) &= \mathbf{K}_o \exp[-i\mathbf{q}(\mathbf{v}(\mathbf{S}_- \circ \mathbf{R}) + \mathbf{x}(m))] \\ &\quad \times \Gamma(\mathbf{q}, \{\mathbf{S}_- \circ \mathbf{R}|\mathbf{v}(\mathbf{S}_- \circ \mathbf{R}) + \mathbf{x}(m)\}) \\ &= \exp[i\mathbf{q}(\mathbf{v}(\mathbf{S}_- \circ \mathbf{R}) + \mathbf{x}(m))] \\ &\quad \times \mathbf{K}_o \Gamma(\mathbf{q}, \{\mathbf{S}_- \circ \mathbf{R}|\mathbf{v}(\mathbf{S}_- \circ \mathbf{R}) + \mathbf{x}(m)\}). \end{aligned} \quad (2.1.3.31)$$

The \mathbf{T} matrix operators provide a *multiplier corepresentation*. The multipliers are not uniquely defined as in equation (2.1.3.21a). Rather, the definition depends on the type and the order of the symmetry operations involved. In order to distinguish between the different kinds of symmetry operations, we introduce the following notation:

$\mathbf{R} \in G_o(\mathbf{q}, -\mathbf{q})$ is an arbitrary element of the point group.
 $\mathbf{R} \in G_o(\mathbf{q})$ is an element of the point group of the wavevector $G_o(\mathbf{q})$ which is a subgroup of $G_o(\mathbf{q}, -\mathbf{q})$. This element is represented by an unitary matrix operator.

$\mathbf{A} \in \mathbf{S}_- \circ G_o(\mathbf{q})$ is an element of the coset $\mathbf{S}_- \circ G_o(\mathbf{q})$, represented by an anti-unitary operator.

The multiplication rule

$$\mathbf{T}(\mathbf{q}, \bar{\mathbf{R}}_i) \mathbf{T}(\mathbf{q}, \bar{\mathbf{R}}_j) = \varphi(\mathbf{q}, \bar{\mathbf{R}}_i, \bar{\mathbf{R}}_j) \mathbf{T}(\mathbf{q}, \bar{\mathbf{R}}_i \circ \bar{\mathbf{R}}_j) \quad (2.1.3.32)$$

is determined by the multipliers

$$\begin{aligned} \varphi(\mathbf{q}, \mathbf{R}_i, \bar{\mathbf{R}}_j) &= \exp[i(\mathbf{q} - \mathbf{R}_i^{-1} \mathbf{q}) \mathbf{v}(\bar{\mathbf{R}}_j)] \\ \varphi(\mathbf{q}, \mathbf{A}_i, \bar{\mathbf{R}}_j) &= \exp[-i(\mathbf{q} + \mathbf{A}_i^{-1} \mathbf{q}) \mathbf{v}(\bar{\mathbf{R}}_j)]. \end{aligned} \quad (2.1.3.33)$$

Again, this representation reduces to an ordinary representation either for symmorphic space groups [all $\mathbf{v}(\bar{\mathbf{R}}_i) = \mathbf{0}$] or for wavevectors within the interior of the Brillouin zone.

All matrix operators of the \mathbf{T} representation commute with the dynamical matrix. Hence, they may be used for the determination of independent elements of the dynamical matrix as well as for the determination of the form of eigenvectors compatible with the atomic structure.

2.1.3.1.1. Example

As an example, we consider a crystal of tetragonal symmetry, space group $P4mm$, with lattice parameters a and c . The primitive cell spanned by the three mutually orthogonal vectors \mathbf{a} , \mathbf{b} and \mathbf{c} contains ten atoms at the positions listed in Table 2.1.3.1 and shown in Fig. 2.1.3.4. Consequently, the dynamical matrix has 30×30 elements.

The space group $P4mm$ contains eight symmetry operations, namely

- (1) the identity, denoted E ;
- (2) a 90° rotation around the z axis, denoted D_{90}^z ;
- (3) a 180° rotation around the z axis, denoted D_{180}^z ;
- (4) a 270° rotation around the z axis, denoted D_{270}^z ;

⁶ The choice of the left coset is arbitrary. We could also consider the right coset $G(\mathbf{q}) \circ \{\mathbf{S}_-|\mathbf{v}(\mathbf{S}_-)\}$. The same enlarged group and the same representations are obtained.

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Table 2.1.3.1. Example structure in space group $P4mm$

Atom No.	x	y	z
1	0	0	0
2	0.5	0.5	0.6
3	0.2	0.1	0
4	0.8	0.9	0
5	0.9	0.8	0
6	0.1	0.8	0
7	0.2	0.9	0
8	0.8	0.1	0
9	0.9	0.2	0
10	0.1	0.2	0

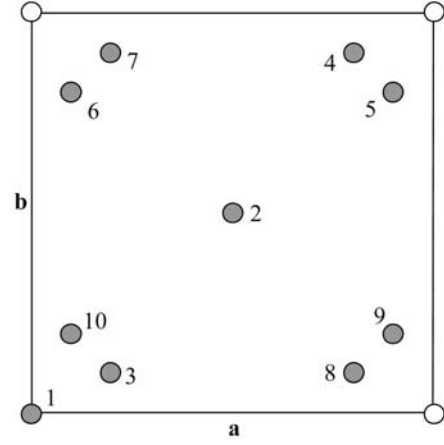


Fig. 2.1.3.4. Projection along the tetragonal z axis of the example structure given in Table 2.1.3.1.

- (5) a mirror plane normal to the x axis, denoted m_x ;
 - (6) a mirror plane normal to the y axis, denoted m_y ;
 - (7) a mirror plane normal to the $[\bar{1}10]$ axis, denoted $m_{[\bar{1}10]}$; and
 - (8) a mirror plane normal to the $[1\bar{1}0]$ axis, denoted $m_{[1\bar{1}0]}$.
- Obviously, atoms No. 3 to 10 are chemically identical and have the same mass.

For the reduction of the dynamical matrix, we need the function $F_o(\kappa, \mathbf{S})$, yielding the label of that atom into which κ is sent by the symmetry operation \mathbf{S} . This function can be represented by the atom transformations shown in Table 2.1.3.2. This table displays the labels of atoms κ and K related by a particular symmetry operation and also the relative position $\mathbf{r}_l - \mathbf{r}_L$ of the primitive cells l and L where both atoms are located. This information is needed for the calculation of phase factors in the expression for the matrix operators \mathbf{T} . Via the twofold axis, atom 6, for example, is transformed into atom 9 located within the cell which is shifted by the vector $-\mathbf{a} - \mathbf{b}$.

Let us first consider the case of phonons with infinite wavelengths and, hence, the symmetry reduction of the dynamical matrix at zero wavevector (the Γ point). Here, the point group of the wavevector is equivalent to the point group $4mm$ of the lattice. According to equation (2.1.3.19a), we can immediately write down the transformation matrix for any of these symmetry operations. Using the notation

$$\begin{aligned}
 \mathbf{E} &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} & \mathbf{D}_{90}^z &= \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \\
 \mathbf{D}_{180}^z &= \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} & \mathbf{D}_{270}^z &= \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \\
 \mathbf{m}_x &= \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} & \mathbf{m}_y &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \\
 \mathbf{m}_{[\bar{1}10]} &= \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} & \mathbf{m}_{[1\bar{1}0]} &= \begin{pmatrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}
 \end{aligned}$$

for the three-dimensional vector representation of the symmetry elements, we obtain the \mathbf{T} matrix operators

$$\mathbf{T}(\mathbf{0}, \mathbf{E}) = \begin{pmatrix} \mathbf{E} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \mathbf{E} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \mathbf{E} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \mathbf{E} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \mathbf{E} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \mathbf{E} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \mathbf{E} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & \mathbf{E} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \mathbf{E} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \mathbf{E} \end{pmatrix}$$

$$\mathbf{T}(\mathbf{0}, \mathbf{D}_{90}^z) = \begin{pmatrix} \mathbf{D}_{90}^z & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \mathbf{D}_{90}^z & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \mathbf{D}_{90}^z & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \mathbf{D}_{90}^z & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \mathbf{D}_{90}^z \\ 0 & 0 & 0 & \mathbf{D}_{90}^z & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \mathbf{D}_{90}^z & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \mathbf{D}_{90}^z \\ 0 & 0 & \mathbf{D}_{90}^z & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \mathbf{D}_{90}^z & 0 & 0 & 0 \end{pmatrix}$$

$$\mathbf{T}(\mathbf{0}, \mathbf{D}_{180}^z) = \begin{pmatrix} \mathbf{D}_{180}^z & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \mathbf{D}_{180}^z & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \mathbf{D}_{180}^z & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \mathbf{D}_{180}^z \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \mathbf{D}_{180}^z & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & \mathbf{D}_{180}^z & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \mathbf{D}_{180}^z & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & \mathbf{D}_{180}^z & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \mathbf{D}_{180}^z & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \mathbf{D}_{180}^z & 0 & 0 & 0 & 0 & 0 \end{pmatrix}$$

Table 2.1.3.2. Atom transformation table

$P4mm$		Symmetry operation							
Atom No.	E	D_{90}^z	D_{180}^z	D_{270}^z	m_x	m_y	$m_{[\bar{1}10]}$	$m_{[1\bar{1}0]}$	
1	1	1	1	1	1	1	1	1	
2	2	2 - \mathbf{a}	2 - $\mathbf{a} - \mathbf{b}$	2 - \mathbf{b}	2 - \mathbf{a}	2 - \mathbf{b}	2	2 - $\mathbf{a} - \mathbf{b}$	
3	3	9 - \mathbf{a}	4 - $\mathbf{a} - \mathbf{b}$	6 - \mathbf{b}	8 - \mathbf{a}	7 - \mathbf{b}	10	5 - $\mathbf{a} - \mathbf{b}$	
4	4	6 - \mathbf{a}	3 - $\mathbf{a} - \mathbf{b}$	9 - \mathbf{b}	7 - \mathbf{a}	8 - \mathbf{b}	5	10 - $\mathbf{a} - \mathbf{b}$	
5	5	7 - \mathbf{a}	10 - $\mathbf{a} - \mathbf{b}$	8 - \mathbf{b}	6 - \mathbf{a}	9 - \mathbf{b}	4	3 - $\mathbf{a} - \mathbf{b}$	
6	6	3 - \mathbf{a}	9 - $\mathbf{a} - \mathbf{b}$	4 - \mathbf{b}	5 - \mathbf{a}	10 - \mathbf{b}	8	7 - $\mathbf{a} - \mathbf{b}$	
7	7	10 - \mathbf{a}	8 - $\mathbf{a} - \mathbf{b}$	5 - \mathbf{b}	4 - \mathbf{a}	3 - \mathbf{b}	9	6 - $\mathbf{a} - \mathbf{b}$	
8	8	5 - \mathbf{a}	7 - $\mathbf{a} - \mathbf{b}$	10 - \mathbf{b}	3 - \mathbf{a}	4 - \mathbf{b}	6	9 - $\mathbf{a} - \mathbf{b}$	
9	9	4 - \mathbf{a}	6 - $\mathbf{a} - \mathbf{b}$	3 - \mathbf{b}	10 - \mathbf{a}	5 - \mathbf{b}	7	8 - $\mathbf{a} - \mathbf{b}$	
10	10	8 - \mathbf{a}	5 - $\mathbf{a} - \mathbf{b}$	7 - \mathbf{b}	9 - \mathbf{a}	6 - \mathbf{b}	3	4 - $\mathbf{a} - \mathbf{b}$	

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$$\mathbf{T}(\mathbf{0}, \mathbf{D}_{270}^z) = \begin{pmatrix} \mathbf{D}_{270}^z & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \mathbf{D}_{270}^z & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \mathbf{D}_{270}^z & 0 \\ 0 & 0 & 0 & 0 & 0 & \mathbf{D}_{270}^z & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \mathbf{D}_{270}^z & 0 & 0 & 0 \\ 0 & 0 & \mathbf{D}_{270}^z & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \mathbf{D}_{270}^z \\ 0 & 0 & 0 & 0 & \mathbf{D}_{270}^z & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \mathbf{D}_{270}^z & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \mathbf{D}_{270}^z & 0 & 0 & 0 \end{pmatrix},$$

$$\mathbf{T}(\mathbf{0}, \mathbf{m}_x) = \begin{pmatrix} \mathbf{m}_x & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \mathbf{m}_x & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & \mathbf{m}_x & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \mathbf{m}_x & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \mathbf{m}_x & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \mathbf{m}_x & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \mathbf{m}_x \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \mathbf{m}_x & 0 \end{pmatrix},$$

$$\mathbf{T}(\mathbf{0}, \mathbf{m}_y) = \begin{pmatrix} \mathbf{m}_y & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \mathbf{m}_y & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \mathbf{m}_y & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & \mathbf{m}_y & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \mathbf{m}_y \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \mathbf{m}_y & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \mathbf{m}_y & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \mathbf{m}_y & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \mathbf{m}_y & 0 & 0 & 0 \end{pmatrix},$$

$$\mathbf{T}(\mathbf{0}, \mathbf{m}_{\bar{1}10}) = \begin{pmatrix} \mathbf{m}_{\bar{1}10} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \mathbf{m}_{\bar{1}10} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \mathbf{m}_{\bar{1}10} \\ 0 & 0 & 0 & 0 & \mathbf{m}_{\bar{1}10} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \mathbf{m}_{\bar{1}10} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & \mathbf{m}_{\bar{1}10} & 0 & \mathbf{m}_y \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \mathbf{m}_{\bar{1}10} & 0 \\ 0 & 0 & 0 & 0 & 0 & \mathbf{m}_{\bar{1}10} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \mathbf{m}_{\bar{1}10} & 0 & 0 & 0 \\ 0 & 0 & \mathbf{m}_{\bar{1}10} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}$$

and

$$\mathbf{T}(\mathbf{0}, \mathbf{m}_{110}) = \begin{pmatrix} \mathbf{m}_{110} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \mathbf{m}_{110} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \mathbf{m}_{110} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \mathbf{m}_{110} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \mathbf{m}_{110} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \mathbf{m}_{110} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \mathbf{m}_{110} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & \mathbf{m}_{110} & 0 & 0 \\ 0 & 0 & 0 & \mathbf{m}_{110} & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}.$$

Since each of these matrices commutes with the dynamical matrix ($\mathbf{T}^{-1} \mathbf{D} \mathbf{T} = \mathbf{D}$, with $\mathbf{T}^{-1} = \mathbf{T}^T$), the following relations are obtained for the $\mathbf{D}_{kk'}(\mathbf{0})$ submatrices:

$$\mathbf{D}_{11}(\mathbf{0}) = \begin{pmatrix} D_{11}^{11} & 0 & 0 \\ 0 & D_{11}^{11} & 0 \\ 0 & 0 & D_{11}^{33} \end{pmatrix},$$

$$\mathbf{D}_{22}(\mathbf{0}) = \begin{pmatrix} D_{22}^{11} & 0 & 0 \\ 0 & D_{22}^{11} & 0 \\ 0 & 0 & D_{22}^{33} \end{pmatrix},$$

$$\mathbf{D}_{13}(\mathbf{0}) = \mathbf{D}_{270}^z \mathbf{D}_{16}(\mathbf{0}) \mathbf{D}_{90}^z = \begin{pmatrix} D_{16}^{22} & -D_{16}^{12} & -D_{16}^{23} \\ -D_{16}^{12} & D_{16}^{11} & D_{16}^{13} \\ -D_{16}^{23} & D_{16}^{13} & D_{16}^{33} \end{pmatrix},$$

$$= \mathbf{D}_{180}^z \mathbf{D}_{14}(\mathbf{0}) \mathbf{D}_{180}^z = \begin{pmatrix} D_{14}^{11} & D_{14}^{12} & -D_{14}^{13} \\ D_{14}^{12} & D_{14}^{22} & -D_{14}^{23} \\ -D_{14}^{13} & -D_{14}^{23} & D_{14}^{33} \end{pmatrix},$$

$$= \mathbf{D}_{90}^z \mathbf{D}_{19}(\mathbf{0}) \mathbf{D}_{270}^z = \begin{pmatrix} D_{19}^{22} & -D_{19}^{12} & D_{19}^{23} \\ -D_{19}^{12} & D_{19}^{11} & -D_{19}^{13} \\ D_{19}^{23} & -D_{19}^{13} & D_{19}^{33} \end{pmatrix},$$

$$= \mathbf{m}_x \mathbf{D}_{18}(\mathbf{0}) \mathbf{m}_x = \begin{pmatrix} D_{18}^{11} & -D_{18}^{12} & -D_{18}^{13} \\ -D_{18}^{12} & D_{18}^{22} & D_{18}^{23} \\ -D_{18}^{13} & D_{18}^{23} & D_{18}^{33} \end{pmatrix},$$

$$= \mathbf{m}_y \mathbf{D}_{17}(\mathbf{0}) \mathbf{m}_y = \begin{pmatrix} D_{17}^{11} & -D_{17}^{12} & D_{17}^{13} \\ -D_{17}^{12} & D_{17}^{22} & -D_{17}^{23} \\ D_{17}^{13} & -D_{17}^{23} & D_{17}^{33} \end{pmatrix},$$

$$= \mathbf{m}_{[\bar{1}10]} \mathbf{D}_{1,10}(\mathbf{0}) \mathbf{m}_{[\bar{1}10]} = \begin{pmatrix} D_{1,10}^{22} & D_{1,10}^{12} & D_{1,10}^{23} \\ D_{1,10}^{12} & D_{1,10}^{11} & D_{1,10}^{13} \\ D_{1,10}^{23} & D_{1,10}^{13} & D_{1,10}^{33} \end{pmatrix},$$

$$= \mathbf{m}_{[110]} \mathbf{D}_{15}(\mathbf{0}) \mathbf{m}_{[110]} = \begin{pmatrix} D_{15}^{22} & D_{15}^{12} & -D_{15}^{23} \\ D_{15}^{12} & D_{15}^{11} & -D_{15}^{13} \\ -D_{15}^{23} & -D_{15}^{13} & D_{15}^{33} \end{pmatrix},$$

and so on for the other submatrices.

For nonzero wavevectors \mathbf{q} along \mathbf{a}^* ($\mathbf{q} = h\mathbf{a}^*$), the point group $G_o(\mathbf{q})$ contains the identity and the mirror plane m_y only. The respective \mathbf{T} matrix operators are the same as for the Γ point:

$$\mathbf{T}(\mathbf{q}, \mathbf{m}_y) = \mathbf{T}(\mathbf{0}, \mathbf{m}_y).$$

There are, however, symmetry elements that invert the wavevector, namely D_{180}^z and m_x . Hence the enlarged group $G_o(\mathbf{q}, -\mathbf{q})$ consists of the elements E , m_y , m_x and D_{180}^z . Inspection of the atom transformation table yields the remaining matrix operators:

$$\mathbf{T}(h\mathbf{a}^*, \mathbf{D}_{180}^z) = \exp(-2\pi i h) \begin{pmatrix} \mathbf{D}_{180}^z \exp(2\pi i h) & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \mathbf{D}_{180}^z & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \mathbf{D}_{180}^z & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \mathbf{D}_{180}^z & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \mathbf{D}_{180}^z \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \mathbf{D}_{180}^z & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \mathbf{D}_{180}^z \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \mathbf{D}_{180}^z & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & \mathbf{D}_{180}^z & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \mathbf{D}_{180}^z & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \mathbf{D}_{180}^z & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \mathbf{K}_o$$

and

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Hence

$$\begin{aligned} D_{11}^{11} &= D_{11}^{11*} = \alpha \quad \text{real} \\ D_{11}^{12} &= -D_{11}^{12} = 0 \\ D_{11}^{13} &= -D_{11}^{13*} = i\beta \quad \text{imaginary} \\ D_{11}^{22} &= D_{11}^{22*} = \gamma \quad \text{real} \\ D_{11}^{23} &= -D_{11}^{23} = 0 \\ D_{11}^{33} &= D_{11}^{33*} = \delta \quad \text{real} \end{aligned} \Rightarrow \mathbf{D}_{11} = \begin{pmatrix} \alpha & 0 & i\beta \\ 0 & \gamma & 0 \\ -i\beta & 0 & \delta \end{pmatrix}.$$

Obviously, the symmetry considerations lead to a remarkable reduction of the independent elements of the dynamical matrix.

2.1.3.2. Symmetry of dispersion planes

According to equation (2.1.3.3), the phonon dispersion is periodic within the reciprocal space:

$$\omega_{(\mathbf{q}+\mathbf{g})j} = \omega_{\mathbf{q}j}. \quad (2.1.3.34)$$

Moreover, for each symmetry operation of the space group of the crystal, the eigenvalue equation may be written in the form

$$\mathbf{D}(\mathbf{S}\mathbf{q}) \mathbf{e}(\mathbf{S}\mathbf{q}, j) = \omega_{(\mathbf{S}\mathbf{q})j}^2 \mathbf{e}(\mathbf{S}\mathbf{q}, j) \quad (2.1.3.35)$$

and due to the transformation property of the dynamical matrix, equation (2.1.3.14),

$$\begin{aligned} \mathbf{D}(\mathbf{q}) \Gamma^+(\mathbf{q}, \{\mathbf{S}|\mathbf{v}(\mathbf{S}) + \mathbf{x}(m)\}) \mathbf{e}(\mathbf{S}\mathbf{q}, j) \\ = \omega_{(\mathbf{S}\mathbf{q})j}^2 \Gamma^+(\mathbf{q}, \{\mathbf{S}|\mathbf{v}(\mathbf{S}) + \mathbf{x}(m)\}) \mathbf{e}(\mathbf{S}\mathbf{q}, j). \end{aligned} \quad (2.1.3.36)$$

Hence $\omega_{(\mathbf{S}\mathbf{q})j}^2$ is an eigenvalue of the dynamical matrix $\mathbf{D}(\mathbf{q})$ at the wavevector \mathbf{q} as is $\omega_{\mathbf{q}j}^2$ itself. If the eigenvalues are not degenerate, *i.e.* if there is not more than one linear independent eigenvector for each eigenvalue, then

$$\omega_{(\mathbf{S}\mathbf{q})j}^2 = \omega_{\mathbf{q}j}^2. \quad (2.1.3.37)$$

If, on the other hand, there are degenerate phonon modes ($\omega_{\mathbf{q}j} = \omega_{\mathbf{q}j'}, j \neq j'$), the most we can strictly infer from equation (2.1.3.36) is

$$\omega_{(\mathbf{S}\mathbf{q})j}^2 = \omega_{\mathbf{q}j}^2. \quad (2.1.3.37a)$$

Without any loss of generality, however, it is possible to label the modes at $\mathbf{S}\mathbf{q}$ in terms of those modes at wavevector \mathbf{q} in such a way that equation (2.1.3.37) remains valid. Hence, we conclude that the phonon dispersion $\omega(\mathbf{q})^9$ in the three-dimensional reciprocal space exhibits the full symmetry of the point group of the crystal, as illustrated in Fig. 2.1.3.5.

Moreover, $\omega_{\mathbf{q}j}$ is an even function of \mathbf{q} (Fig. 2.1.3.6). This is always true even if the space group does not contain the inversion, since the dynamical matrix is Hermitian. From the eigenvector equation (2.1.2.20) we have

$$\mathbf{D}(-\mathbf{q}) \mathbf{e}(-\mathbf{q}, j) = \mathbf{D}^*(\mathbf{q}) \mathbf{e}(-\mathbf{q}, j) = \omega_{-\mathbf{q}j}^2 \mathbf{e}(-\mathbf{q}, j). \quad (2.1.3.38)$$

Taking the complex conjugate and remembering that the eigenvalues of a Hermitian matrix are real quantities,

$$\mathbf{D}(\mathbf{q}) \mathbf{e}^*(-\mathbf{q}, j) = \omega_{-\mathbf{q}j}^2 \mathbf{e}^*(-\mathbf{q}, j). \quad (2.1.3.38a)$$

Obviously, $\omega_{-\mathbf{q}j}^2$ is an eigenvalue of $\mathbf{D}(\mathbf{q})$ just as $\omega_{\mathbf{q}j}^2$ is. Hence, with the same arguments as above we conclude that

$$\omega_{-\mathbf{q}j} = \omega_{\mathbf{q}j}. \quad (2.1.3.39)$$

⁹ Note that we always choose the positive root $\omega(\mathbf{q}) = +\sqrt{\omega^2(\mathbf{q})}$ for the phonon frequency.

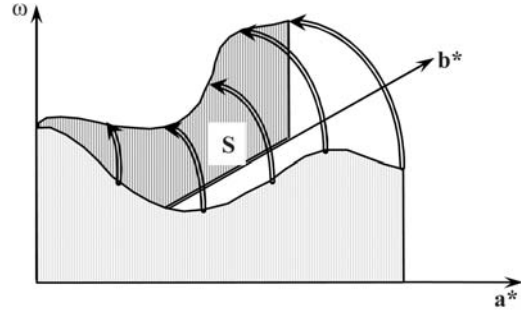


Fig. 2.1.3.5. Symmetry of the dispersion surface.

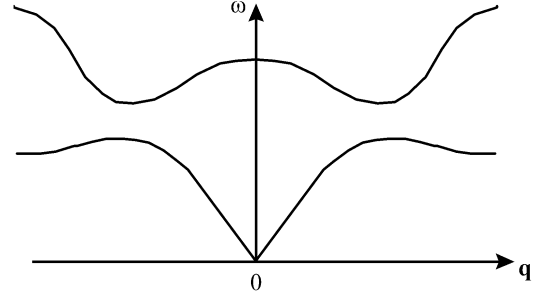


Fig. 2.1.3.6. The dispersion relation is an even function of \mathbf{q} .

2.1.3.3. Symmetry properties of eigenvectors

In the previous section we used the symmetry properties of the dynamical matrix to derive equation (2.1.3.36). Since the phonon dispersion $\omega(\mathbf{q}, j)$ is invariant with respect to all symmetry operations $\{\mathbf{S}|\mathbf{v}(\mathbf{S}) + \mathbf{x}(m)\}$ of the space group [equation (2.1.3.37)], we conclude that not only is $\mathbf{e}(\mathbf{q}, j)$ an eigenvector of the dynamical matrix $\mathbf{D}(\mathbf{q})$ but so is the vector $\Gamma^+(\mathbf{q}, \{\mathbf{S}|\mathbf{v}(\mathbf{S}) + \mathbf{x}(m)\}) \mathbf{e}(\mathbf{S}\mathbf{q}, j)$. If the corresponding eigenvalue $\omega_{\mathbf{q}j}^2$ is not degenerate, the (normalized) eigenvectors are uniquely determined except for a phase factor of unit modulus. Hence, the following relation holds:

$$\begin{aligned} \mathbf{e}(\mathbf{S}\mathbf{q}, j) &= \exp(i\varphi) \Gamma(\mathbf{q}, \{\mathbf{S}|\mathbf{v}(\mathbf{S}) + \mathbf{x}(m)\}) \mathbf{e}(\mathbf{q}, j) \\ &= \exp(i\varphi) \Gamma(\mathbf{S}\mathbf{q}, \{\mathbf{E}|\mathbf{x}(m)\}) \Gamma(\mathbf{q}, \{\mathbf{S}|\mathbf{v}(\mathbf{S})\}) \mathbf{e}(\mathbf{q}, j) \\ &= \exp(i\varphi) \exp[-i(\mathbf{S}\mathbf{q}) \cdot \mathbf{x}(m)] \Gamma(\mathbf{q}, \{\mathbf{S}|\mathbf{v}(\mathbf{S})\}) \mathbf{e}(\mathbf{q}, j). \end{aligned} \quad (2.1.3.40)$$

The statement giving the atomic displacements as solutions of the equations of motion (*cf.* Section 2.1.2) was based on Bloch waves, the polarization vector being invariant with respect to lattice translations. It is therefore convenient to choose the arbitrary phase factor in the transformation law for eigenvectors in such a way as to leave the right-hand side of equation (2.1.3.40) independent of $\mathbf{x}(m)$. Setting the phase angle φ equal to $(\mathbf{S}\mathbf{q}) \cdot \mathbf{x}(m)$, we obtain the simple form of the transformation law

$$\mathbf{e}(\mathbf{S}\mathbf{q}, j) = \Gamma(\mathbf{q}, \{\mathbf{S}|\mathbf{v}(\mathbf{S})\}) \mathbf{e}(\mathbf{q}, j). \quad (2.1.3.41)$$

This choice is, however, not always possible. If there is a symmetry operation \mathbf{S}_- that inverts the wavevector, then in addition to equation (2.1.3.40) there is another relation between $\mathbf{e}(-\mathbf{q}, j)$ and $\mathbf{e}(\mathbf{q}, j)$ due to the Hermitian nature of the dynamical matrix. Hence in this case the transformation law may differ from equation (2.1.3.41), as discussed in Section 2.1.3.5.2.

If the dynamical matrix exhibits degenerate eigenvalues for the wavevector \mathbf{q} , the most that can be said is that the symmetry operation $\{\mathbf{S}|\mathbf{v}(\mathbf{S}) + \mathbf{x}(m)\}$ sends an eigenvector $\mathbf{e}(\mathbf{q}, j)$ into some linear combination of all those eigenvectors that correspond to the same eigenvalue. Without any loss of generality we may,

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however, demand that equation (2.1.3.41) remains valid even in this case, since if we would have determined eigenvectors $\mathbf{e}(\mathbf{q}, j)$ at \mathbf{q} then among the variety of possible and equivalent orthonormal sets of eigenvectors at $\mathbf{S}\mathbf{q}$ we simply choose that particular one which is given by (2.1.3.41). There is, however, one exception, which applies to wavevectors on the Brillouin-zone boundary and symmetry operations with $\mathbf{S}\mathbf{q} = \mathbf{q} + \mathbf{g}$ (where \mathbf{g} is a reciprocal-lattice vector): owing to the periodicity $\mathbf{e}(\mathbf{q} + \mathbf{g}, j) = \mathbf{e}(\mathbf{q}, j)$, equation (2.1.3.3), the eigenvectors $\mathbf{e}(\mathbf{S}\mathbf{q}, j)$ and $\mathbf{e}(\mathbf{q}, j)$ have to be identical in this case.

If we consider those symmetry operations that leave the wavevector invariant (except for an additional reciprocal-lattice vector), we are able to obtain special conditions for the eigenvectors themselves. In Section 2.1.3.1 we found that the dynamical matrix commutes with the \mathbf{T} matrix operators defined by equation (2.1.3.19a). Hence, if \mathbf{R} is an arbitrary element of the point group $G_o(\mathbf{q})$, the vector $\mathbf{T}(\mathbf{q}, \mathbf{R})\mathbf{e}(\mathbf{q}, j)$ is an eigenvector with respect to the eigenvalue $\omega_{\mathbf{q},j}^2$ as well as $\mathbf{e}(\mathbf{q}, j)$:

$$\mathbf{D}(\mathbf{q}) \{\mathbf{T}(\mathbf{q}, \mathbf{R})\mathbf{e}(\mathbf{q}, j)\} = \omega_{\mathbf{q},j}^2 \{\mathbf{T}(\mathbf{q}, \mathbf{R})\mathbf{e}(\mathbf{q}, j)\}. \quad (2.1.3.42)$$

Since eigenvalues may be degenerate, we now replace the index j that labels the $3N$ different phonon branches by the double index $\sigma\lambda$: σ labels all different eigenvalues whereas λ distinguishes those phonons that are degenerate by symmetry,¹⁰ *i.e.* that have the same frequency but different eigenvectors,

$$j \rightarrow \sigma, \lambda.$$

λ runs from 1 to f_σ if f_σ is the degeneracy of the eigenfrequency $\omega_{\mathbf{q},\sigma}$. With this notation, equation (2.1.3.42) can be rewritten as

$$\mathbf{D}(\mathbf{q}) \{\mathbf{T}(\mathbf{q}, \mathbf{R})\mathbf{e}(\mathbf{q}, \sigma\lambda)\} = \omega_{\mathbf{q},\sigma}^2 \{\mathbf{T}(\mathbf{q}, \mathbf{R})\mathbf{e}(\mathbf{q}, \sigma\lambda)\}. \quad (2.1.3.42a)$$

Consequently, the vector $\mathbf{T}(\mathbf{q}, \mathbf{R})\mathbf{e}(\mathbf{q}, \sigma\lambda)$ has to be some linear combination of all eigenvectors $\mathbf{e}(\mathbf{q}, \sigma\lambda')$, $\lambda' = 1, \dots, f_\sigma$, corresponding to the same eigenvalue $\omega_{\mathbf{q},\sigma}^2$,

$$\mathbf{T}(\mathbf{q}, \mathbf{R})\mathbf{e}(\mathbf{q}, \sigma\lambda) = \sum_{\lambda'=1}^{f_\sigma} \tau_{\lambda\lambda'}^{(\sigma)}(\mathbf{q}, \mathbf{R})\mathbf{e}(\mathbf{q}, \sigma\lambda'). \quad (2.1.3.43)$$

Obviously, the eigenvectors $\mathbf{e}(\mathbf{q}, \sigma\lambda)$ ($\lambda = 1, \dots, f_\sigma$) span a vector space that is invariant with respect to all symmetry operations of the point group of the wavevector. Moreover, this vector space does not contain any proper invariant subspaces and is therefore *irreducible*. Under the symmetry operations of the group $G_o(\mathbf{q})$, the f_σ eigenvectors transform into each other. The corresponding coefficients $\tau_{\lambda\lambda'}^{(\sigma)}(\mathbf{q}, \mathbf{R})$ can be regarded as the elements of a complex ($f_\sigma \times f_\sigma$) matrix $\boldsymbol{\tau}^{(\sigma)}(\mathbf{q}, \mathbf{R})$ that induces a unitary irreducible multiplier representation (IMR) of the point group of the wavevector. The complex multiplier is exactly the same as for the $3N$ -dimensional reducible representation provided by the \mathbf{T} matrix operators [*cf.* equation (2.1.3.21)].

For a given point group $G_o(\mathbf{q})$ there is only a limited number of irreducible representations. These can be calculated by group-theoretical methods and are tabulated, for example, in the monographs of Kovalev (1965) or Bradley & Cracknell (1972). The multipliers are specific for the individual space groups $G(\mathbf{q})$ and depend merely on the fractional translations $\mathbf{v}(\mathbf{R})$ associated with a symmetry element \mathbf{R} . It should be noted that for wavevectors within the Brillouin zone and for symmorphic space groups all multipliers are unity and we are left with ordinary irreducible representations. Hence, merely on the basis of group-theoretical considerations, restrictions for the phonon eigenvectors can be obtained.

A particular phonon can now be characterized by the symmetry of the corresponding eigenvector, *i.e.* the irreducible

multiplier representation (IMR) that describes its transformation behaviour. All degenerate phonons obviously belong to the same IMR. Moreover, phonons with different frequencies may belong to the same IMR. On the other hand, there may also be IMRs to which no phonon belongs at all. For a given crystalline structure it is possible, however, to predict the number of phonons with eigenvectors transforming according to a particular irreducible multiplier representation:

Let us arrange all eigenvectors $\mathbf{e}(\mathbf{q}, \sigma\lambda)$ of the dynamical matrix as columns of a unitary matrix $\mathbf{e}(\mathbf{q})$ in such a way that eigenvectors of the same irreducible representation occupy neighbouring columns:

$$\mathbf{e}(\mathbf{q}) = (\mathbf{e}(\mathbf{q}, 11) \dots \mathbf{e}(\mathbf{q}, 1f_1)\mathbf{e}(\mathbf{q}, 21) \dots \mathbf{e}(\mathbf{q}, 2f_2) \dots). \quad (2.1.3.44)$$

This matrix can now be used for a similarity transformation of the \mathbf{T} matrix operators:

$$\mathbf{e}(\mathbf{q})^{-1} \mathbf{T}(\mathbf{q}, \mathbf{R}) \mathbf{e}(\mathbf{q}) = \Delta(\mathbf{q}, \mathbf{R}). \quad (2.1.3.45)$$

Since an eigenvector can never change its symmetry by the multiplication with the \mathbf{T} matrix operator and since all eigenvectors are pairwise orthonormal, the resulting matrix $\Delta(\mathbf{q}, \mathbf{R})$ has block-diagonal form. Moreover, each block on the diagonal consists of the matrix of a particular irreducible multiplier representation:

$$\Delta(\mathbf{q}, \mathbf{R}) = \begin{pmatrix} \boldsymbol{\tau}^{(1)}(\mathbf{q}, \mathbf{R}) & 0 & s & 0 & 0 \\ 0 & \boldsymbol{\tau}^{(2)}(\mathbf{q}, \mathbf{R}) & s & 0 & 0 \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & 0 & 0 & \ddots & 0 \\ 0 & 0 & 0 & 0 & \ddots \end{pmatrix}. \quad (2.1.3.46)$$

The matrix of eigenvectors thus reduces the operators \mathbf{T} to block-diagonal form.

There may be several phonons with different frequencies that belong to the same symmetry (irreducible representation). All purely longitudinally polarized lattice vibrations, irrespective of whether these are acoustic or optic modes, belong to the totally symmetric representation. This is because each vector parallel to \mathbf{q} – and in purely longitudinal modes the polarization vectors of each individual atom are parallel to the wavevector – is left invariant by any of the symmetry elements of $G_o(\mathbf{q})$. A particular irreducible representation may thus appear more than once in the decomposition of the \mathbf{T} matrix and, consequently, two or more of the blocks within the matrix $\Delta(\mathbf{q}, \mathbf{R})$ may be identical. Therefore, it is convenient to split the index σ that labels the modes of different frequency into two indices s and a ,

$$\sigma \rightarrow s, a.$$

s characterizes the inequivalent irreducible multiplier representations and a is the running index over all modes of the same symmetry but of different frequency. If c_s denotes the multiplicity of the representation s , then a takes the values $1, \dots, c_s$. Using this notation, the transformation law for the eigenvectors can be rewritten as

$$\mathbf{T}(\mathbf{q}, \mathbf{R})\mathbf{e}(\mathbf{q}, sa\lambda) = \sum_{\lambda'=1}^{f_s} \tau_{\lambda\lambda'}^{(s)}(\mathbf{q}, \mathbf{R})\mathbf{e}(\mathbf{q}, sa\lambda') \quad \text{for } \lambda = 1, \dots, f_s \text{ and } a = 1, \dots, c_s. \quad (2.1.3.47)$$

As a well known result from group theory, the multiplicity c_s of a particular irreducible multiplier representation s in the decomposition of the reducible $3N$ -dimensional \mathbf{T} -matrix representation can be calculated from the respective characters

¹⁰ Accidental degeneracies that are due to the specific strength of interatomic forces are not considered here.

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$$\begin{aligned}\chi(\mathbf{q}, \mathbf{R}) &= \sum_{\kappa\alpha} T_{\kappa\kappa}^{\alpha\alpha}(\mathbf{q}, \mathbf{R}) \\ &= \sum_{\kappa\alpha} R_{\alpha\alpha} \delta(\kappa, F_o(\kappa, \mathbf{R})) \exp[i\mathbf{q}(\mathbf{r}_\kappa - \mathbf{R}\mathbf{r}_\kappa)]\end{aligned}\quad (2.1.3.48)$$

and

$$\chi^{(s)}(\mathbf{q}, \mathbf{R}) = \sum_{\lambda=1}^{f_s} \tau_{\lambda\lambda}^{(s)}(\mathbf{q}, \mathbf{R}) \quad (2.1.3.49)$$

according to

$$c_s = (1/|G|) \sum_{\mathbf{R}} \chi(\mathbf{q}, \mathbf{R}) \chi^{(s)*}(\mathbf{q}, \mathbf{R}). \quad (2.1.3.50)$$

The summation index runs over all symmetry elements of the point group $G_o(\mathbf{q})$, the order of which is denoted by $|G|$. Hence we are able to predict the number of non-degenerate phonon modes for any of the different irreducible multiplier representations on the basis of group-theoretical considerations. Obviously, there are exactly $c_s \times f_s$ modes with eigenvectors that transform according to the irreducible multiplier representation s . Among these, groups of always f_s phonons have the same frequency. *The degeneracy corresponds to the dimensionality of the irreducible representation.* The crystallographic space groups give rise to one-, two- or three-dimensional irreducible representations. A maximum of three fundamental lattice vibrations can therefore be degenerate by symmetry, a situation that is observed for some prominent wavevectors within cubic crystals.

Symmetry considerations not only provide a means for a concise labelling of phonons; group theory can also be used to predict the form of eigenvectors that are compatible with the lattice structure. This aspect leads to the concept of symmetry coordinates, which is presented in Section 2.1.3.4.

2.1.3.3.1. Example

Let us return to the example presented in Section 2.1.3.1.1. At the Γ point, the point group of the wavevector is identical to the point group of the crystal, namely $4mm$. It contains all eight symmetry operations and there are five different irreducible representations, denoted $\tau^{(1+)}$, $\tau^{(1-)}$, $\tau^{(3+)}$, $\tau^{(3-)}$ and $\tau^{(2)}$. The corresponding character table including the reducible representation provided by the \mathbf{T} -matrix operators (*cf.* Section 2.1.3.1.1) has the form shown in Table 2.1.3.3. The representations $\tau^{(1+)}$, $\tau^{(1-)}$, $\tau^{(3+)}$ and $\tau^{(3-)}$ are one-dimensional, and $\tau^{(2)}$ is two-dimensional. The upper index, + or -, refers to the symmetry with respect to the mirror plane m_x . According to (2.1.3.50), we may calculate the multiplicities of these irreducible representations in the decomposition of the 30-dimensional \mathbf{T} representation. As the result we obtain

$$c_{\tau^{(1+)}} = 5, \quad c_{\tau^{(1-)}} = 3, \quad c_{\tau^{(3+)}} = 3, \quad c_{\tau^{(3-)}} = 3, \quad c_{\tau^{(2)}} = 8.$$

Hence for the sample structure presented in Section 2.1.3.1.1 we expect to have five phonon modes of symmetry $\tau^{(1+)}$, three modes

for each of the symmetries $\tau^{(1-)}$, $\tau^{(3+)}$ and $\tau^{(3-)}$, and 16 modes of symmetry $\tau^{(2)}$, the latter being divided into pairs of doubly degenerate phonons.

2.1.3.4. Symmetry coordinates

So far, we have used the $3N$ Cartesian coordinates of all atoms within a primitive cell in order to describe the dynamics of the crystal lattice. Within this coordinate system, the elements of the dynamical matrix can be calculated on the basis of specific models for interatomic interactions. The corresponding eigenvectors or normal coordinates are some linear combinations of the Cartesian components. With respect to these normal coordinates, which are specific to each particular crystal, the dynamical matrix has diagonal form and contains the squares of the eigenfrequencies reflecting the interatomic forces.

As shown in Sections 2.1.3.1 and 2.1.3.3, there are constraints for the dynamical matrix due to the symmetry of the crystal lattice and, hence, eigenvectors must obey certain transformation laws. Not all arbitrary linear combinations of the Cartesian coordinates can form an eigenvector. Rather, there are *symmetry-adapted coordinates* or simply *symmetry coordinates* compatible with a given structure that can be used to predict the general form of eigenvectors without the need for any particular model of interatomic interactions. These symmetry coordinates can be determined on the basis of the irreducible multiplier representations introduced in the previous section.

From the \mathbf{T} -matrix operators and the representation matrices $\tau^{(s)}(\mathbf{q}, \mathbf{R})$ of a particular irreducible multiplier representation we may define another matrix operator $\mathbf{P}^{(s)}(\mathbf{q})$ with the elements

$$\mathbf{P}_{\lambda\lambda'}^{(s)}(\mathbf{q}) = (f_s/|G|) \sum_{\mathbf{R}} \tau_{\lambda\lambda'}^{(s)*}(\mathbf{q}, \mathbf{R}) \mathbf{T}(\mathbf{q}, \mathbf{R}). \quad (2.1.3.51)$$

When applied to an arbitrary $3N$ -dimensional vector Ψ built from the Cartesian coordinates of the individual atoms, this operator yields the particular component of Ψ that transforms according to the irreducible representation s . Hence it acts as a *projection operator*. Defining a set of f_s vectors by

$$\mathbf{E}(\mathbf{q}, s\lambda) = \mathbf{P}_{\lambda\lambda'}^{(s)}(\mathbf{q}) \Psi, \quad \lambda = 1, \dots, f_s, \quad (2.1.3.52)$$

we obtain

$$\mathbf{T}(\mathbf{q}, \mathbf{R}') \mathbf{E}(\mathbf{q}, s\lambda) = (f_s/|G|) \sum_{\mathbf{R}} \tau_{\lambda\lambda'}^{(s)*}(\mathbf{q}, \mathbf{R}) \mathbf{T}(\mathbf{q}, \mathbf{R}') \mathbf{T}(\mathbf{q}, \mathbf{R}) \Psi. \quad (2.1.3.53)$$

Using the multiplication rule (2.1.3.21a), it can be shown that the right-hand side of this equation reduces to

$$(f_s/|G|) \sum_{\mathbf{R}} \sum_{\lambda''=1}^{f_s} \tau_{\lambda''\lambda}^{(s)}(\mathbf{q}, \mathbf{R}') \tau_{\lambda''\lambda'}^{(s)*}(\mathbf{q}, \mathbf{R}' \circ \mathbf{R}) \mathbf{T}(\mathbf{q}, \mathbf{R}' \circ \mathbf{R}) \Psi,$$

which can also be written in the form

Table 2.1.3.3. Character table of the point group $4mm$

$4mm$	Symmetry operation							
	E	D_{90}^z	D_{180}^z	D_{270}^z	m_x	m_y	$m_{[110]}$	$m_{[1\bar{1}0]}$
X_T	30	2	-2	2	2	2	2	2
$X_{\tau^{(1+)}}$	1	1	1	1	1	1	1	1
$X_{\tau^{(1-)}}$	1	1	1	1	-1	-1	-1	-1
$X_{\tau^{(3+)}}$	1	-1	1	-1	1	1	-1	-1
$X_{\tau^{(3-)}}$	1	-1	1	-1	-1	-1	1	1
$\tau^{(2)}$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} i & 0 \\ 0 & -i \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} -i & 0 \\ 0 & i \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$	$\begin{pmatrix} 1 & i \\ -i & 0 \end{pmatrix}$
$X_{\tau^{(2)}}$	2	0	-2	0	0	0	0	0

2. SYMMETRY ASPECTS OF EXCITATIONS

$$\sum_{\lambda''=1}^{f_s} \tau_{\lambda''\lambda}^{(s)}(\mathbf{q}, \mathbf{R}') (f_s/|G|) \sum_{\mathbf{R}} \tau_{\lambda''\lambda'}^{(s)*}(\mathbf{q}, \mathbf{R}) \mathbf{T}(\mathbf{q}, \mathbf{R}) \Psi,$$

since if \mathbf{R} runs over all symmetry operations of the group $G_o(\mathbf{q})$ the same is true for the product $\mathbf{R}' \circ \mathbf{R}$. Comparing this expression with the definitions (2.1.3.51) and (2.1.3.52) we obtain

$$\mathbf{T}(\mathbf{q}, \mathbf{R}') \mathbf{E}(\mathbf{q}, s\lambda) = \sum_{\lambda''=1}^{f_s} \tau_{\lambda''\lambda}^{(s)}(\mathbf{q}, \mathbf{R}') \mathbf{E}(\mathbf{q}, s\lambda''). \quad (2.1.3.54)$$

Hence the set of vectors $\mathbf{E}(\mathbf{q}, s\lambda)$ span an irreducible vector space and transform into each other in just the same way as the eigenvectors $\mathbf{e}(\mathbf{q}, sa\lambda)$ of the dynamical matrix do.

If the corresponding irreducible representation s appears only once in the decomposition of the $3N$ -dimensional \mathbf{T} representation, then the vector space provided by the $\mathbf{E}(\mathbf{q}, s\lambda)$, $\lambda = 1, \dots, f_s$, is uniquely determined. Consequently, these basis vectors themselves may be regarded as eigenvectors of the dynamical matrix. In this case, symmetry considerations alone determine the polarization of lattice vibrations irrespective of the particular interatomic interactions.

If, on the other hand, the multiplicity c_s of the representation s is larger than 1, the most that can be inferred is that each of the vectors $\mathbf{E}(\mathbf{q}, s\lambda)$ is some linear combination of the c_s eigenvectors $\mathbf{e}(\mathbf{q}, sa\lambda)$, $a = 1, \dots, c_s$. By an appropriate choice of the different generating vectors Ψ_a in (2.1.3.52), it is, however, always possible to find a set of c_s pairwise orthogonal vectors $\mathbf{E}(\mathbf{q}, sa\lambda)$ that span the same vector space as the eigenvectors $\mathbf{e}(\mathbf{q}, sa\lambda)$. If we repeat this procedure for every irreducible representation s contributing to the \mathbf{T} representation, we obtain $3N$ linearly independent vectors, the *symmetry coordinates*, that generate a new coordinate system within the $3N$ -dimensional space of atomic displacements. With respect to this coordinate system the dynamical matrix is reduced to a symmetry-adapted block-diagonal form.

In order to show this, let us denote the matrix elements of the transformed dynamical matrix by $\bar{D}_{sa\lambda}^{s'a'\lambda'}(\mathbf{q})$ ($\lambda = 1, \dots, f_s$, $a = 1, \dots, c_s$) and the components of the symmetry coordinates by $E_{\kappa}^{\alpha}(\mathbf{q}, sa\lambda)$ ($\kappa = 1, \dots, N$, $\alpha = 1, 2, 3$). Then the following equation holds, since the dynamical matrix $\mathbf{D}(\mathbf{q})$ commutes with the \mathbf{T} -matrix operators and since the symmetry coordinates transform according to (2.1.3.54):

$$\begin{aligned} \bar{D}_{sa\lambda}^{s'a'\lambda'}(\mathbf{q}) &= \sum_{\kappa\alpha} \sum_{\kappa'\beta} E_{\kappa}^{\alpha*}(\mathbf{q}, sa\lambda) D_{\kappa\kappa'}^{\alpha\beta}(\mathbf{q}) E_{\kappa'}^{\beta}(\mathbf{q}, s'a'\lambda') \\ &= \sum_{\kappa\alpha} \sum_{\kappa'\beta} E_{\kappa}^{\alpha*}(\mathbf{q}, sa\lambda) \\ &\quad \times \sum_{\kappa_1\alpha_1} \sum_{\kappa_2\alpha_2} \{ (T^{-1}(\mathbf{q}, \mathbf{R}))_{\kappa\kappa_1}^{\alpha\alpha_1} D_{\kappa_1\kappa_2}^{\alpha_1\alpha_2}(\mathbf{q}) (T(\mathbf{q}, \mathbf{R}))_{\kappa_2\kappa'}^{\alpha_2\beta} \} \\ &\quad \times E_{\kappa'}^{\beta}(\mathbf{q}, s'a'\lambda') \\ &= \sum_{\kappa_1\alpha_1} \sum_{\kappa_2\alpha_2} \sum_{\mu=1}^{f_s} \sum_{\mu'=1}^{f_s} \tau_{\mu\lambda}^{(s)*}(\mathbf{q}, \mathbf{R}) E_{\kappa_1}^{\alpha_1}(\mathbf{q}, sa\mu) \\ &\quad \times D_{\kappa_1\kappa_2}^{\alpha_1\alpha_2}(\mathbf{q}) \tau_{\mu'\lambda'}^{(s')}(\mathbf{q}, \mathbf{R}) E_{\kappa_2}^{\alpha_2}(\mathbf{q}, s'a'\lambda') \\ &= \sum_{\mu=1}^{f_s} \sum_{\mu'=1}^{f_s} \tau_{\mu\lambda}^{(s)*}(\mathbf{q}, \mathbf{R}) \tau_{\mu'\lambda'}^{(s')}(\mathbf{q}, \mathbf{R}) \bar{D}_{sa\mu}^{s'a'\mu'}(\mathbf{q}). \end{aligned} \quad (2.1.3.55)$$

Owing to the orthogonality of the irreducible representation, we obtain after summation over all symmetry elements \mathbf{R} and division by the order of the group

$$\begin{aligned} \bar{D}_{sa\lambda}^{s'a'\lambda'}(\mathbf{q}) &= (1/|G|) \sum_{\mathbf{R}} \sum_{\mu=1}^{f_s} \sum_{\mu'=1}^{f_s} \tau_{\mu\lambda}^{(s)*}(\mathbf{q}, \mathbf{R}) \tau_{\mu'\lambda'}^{(s')}(\mathbf{q}, \mathbf{R}) \bar{D}_{sa\mu}^{s'a'\mu'}(\mathbf{q}) \\ &= (1/f_s) \sum_{\mu=1}^{f_s} \sum_{\mu'=1}^{f_s} \delta_{\mu\mu'} \delta_{\lambda\lambda'} \delta_{ss'} \bar{D}_{sa\mu}^{s'a'\mu'}(\mathbf{q}) \\ &= (1/f_s) \delta_{\lambda\lambda'} \delta_{ss'} \sum_{\mu=1}^{f_s} \bar{D}_{sa\mu}^{s'a'\mu'}(\mathbf{q}). \end{aligned} \quad (2.1.3.56)$$

This equation proves the block-diagonal form of the transformed dynamical matrix $\bar{\mathbf{D}}$. Hence, with respect to the symmetry coordinates, the dynamical matrix can be represented by submatrices $\bar{\mathbf{D}}^{(s)}(\mathbf{q})$ of dimension $c_s \times c_s$ that are determined by the individual irreducible representations (s):

$$\bar{\mathbf{D}}(\mathbf{q}) = \begin{pmatrix} \bar{\mathbf{D}}^{(1)}(\mathbf{q}) & \mathbf{0} & s & \mathbf{0} \\ \mathbf{0} & \bar{\mathbf{D}}^{(2)}(\mathbf{q}) & s & \mathbf{0} \\ \vdots & \vdots & \ddots & \vdots \\ \mathbf{0} & \mathbf{0} & s & \ddots \end{pmatrix}. \quad (2.1.3.57)$$

The elements of the submatrices are given by

$$\bar{D}_{aa'}^{(s)}(\mathbf{q}) = \sum_{\kappa\alpha} \sum_{\kappa'\beta} E_{\kappa}^{\alpha*}(\mathbf{q}, sa\lambda) D_{\kappa\kappa'}^{\alpha\beta}(\mathbf{q}) E_{\kappa'}^{\beta}(\mathbf{q}, sa'\lambda), \quad (2.1.3.58)$$

and must be independent of λ . Obviously, a submatrix $\bar{\mathbf{D}}^{(s)}(\mathbf{q})$ may appear once, twice or three times on the diagonal, according to the dimensionality f_s of the respective irreducible representation.

The eigenvectors and eigenvalues of the block-diagonalized dynamical matrix can be collected from the eigenvectors and eigenvalues of the individual submatrices. Hence, the eigenvectors of $\bar{\mathbf{D}}^{(s)}(\mathbf{q})$ correspond to the c_s non-degenerate phonons of symmetry s .

2.1.3.4.1. Example

Let us try to find the symmetry coordinates corresponding to our sample structure introduced in Section 2.1.3.1.1 for $\mathbf{q} = \mathbf{0}$. Using the irreducible representations displayed in Section 2.1.3.3.1, we write down the projection operator for representation $\tau^{(1\pm)}$ according to equation (2.1.3.51):

$$\mathbf{P}_{11}^{(1\pm)}(\mathbf{0}) = \frac{1}{8} \begin{pmatrix} \Sigma_1^{\pm} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \Sigma_1^{\pm} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \mathbf{E} & \mathbf{D}_{180}^z & \pm \mathbf{m}_{[110]} & \mathbf{D}_{90}^z & \pm \mathbf{m}_x & \pm \mathbf{m}_y & \mathbf{D}_{270}^z & \pm \mathbf{m}_{[110]} \\ 0 & 0 & \mathbf{D}_{180}^z & \mathbf{E} & \pm \mathbf{m}_{[110]} & \mathbf{D}_{270}^z & \pm \mathbf{m}_x & \pm \mathbf{m}_y & \mathbf{D}_{90}^z & \pm \mathbf{m}_{[110]} \\ 0 & 0 & \pm \mathbf{m}_{[110]} & \pm \mathbf{m}_{[110]} & \mathbf{E} & \pm \mathbf{m}_x & \mathbf{D}_{270}^z & \mathbf{D}_{90}^z & \pm \mathbf{m}_y & \mathbf{D}_{180}^z \\ 0 & 0 & \mathbf{D}_{270}^z & \mathbf{D}_{90}^z & \pm \mathbf{m}_x & \mathbf{E} & \pm \mathbf{m}_{[110]} & \pm \mathbf{m}_{[110]} & \mathbf{D}_{180}^z & \pm \mathbf{m}_y \\ 0 & 0 & \pm \mathbf{m}_y & \pm \mathbf{m}_x & \mathbf{D}_{90}^z & \pm \mathbf{m}_{[110]} & \mathbf{E} & \mathbf{D}_{180}^z & \pm \mathbf{m}_{[110]} & \mathbf{D}_{270}^z \\ 0 & 0 & \pm \mathbf{m}_x & \pm \mathbf{m}_y & \mathbf{D}_{270}^z & \pm \mathbf{m}_{[110]} & \mathbf{D}_{180}^z & \mathbf{E} & \pm \mathbf{m}_{[110]} & \mathbf{D}_{90}^z \\ 0 & 0 & \mathbf{D}_{90}^z & \mathbf{D}_{270}^z & \pm \mathbf{m}_y & \mathbf{D}_{180}^z & \pm \mathbf{m}_{[110]} & \pm \mathbf{m}_{[110]} & \mathbf{E} & \pm \mathbf{m}_x \\ 0 & 0 & \pm \mathbf{m}_{[110]} & \pm \mathbf{m}_{[110]} & \mathbf{D}_{180}^z & \pm \mathbf{m}_y & \mathbf{D}_{90}^z & \mathbf{D}_{270}^z & \pm \mathbf{m}_x & \mathbf{E} \end{pmatrix}$$

with the abbreviations

$$\begin{aligned} \Sigma_1^+ &= \mathbf{E} + \mathbf{D}_{90}^z + \mathbf{D}_{180}^z + \mathbf{D}_{270}^z + \mathbf{m}_x + \mathbf{m}_y + \mathbf{m}_{[110]} + \mathbf{m}_{[110]} \\ &= \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 8 \end{pmatrix}, \\ \Sigma_1^- &= \mathbf{E} + \mathbf{D}_{90}^z + \mathbf{D}_{180}^z + \mathbf{D}_{270}^z - \mathbf{m}_x - \mathbf{m}_y - \mathbf{m}_{[110]} - \mathbf{m}_{[110]} \\ &= \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} = \mathbf{0}. \end{aligned}$$

2.1. PHONONS

From the results in Section 2.1.3.4, we expect to have five symmetry coordinates corresponding to representation $\tau^{(1+)}$ and three for $\tau^{(1-)}$ according to the respective multiplicities. Let $\mathbf{x}_1, \mathbf{y}_1, \mathbf{z}_1, \mathbf{x}_2, \mathbf{y}_2, \mathbf{z}_2, \dots, \mathbf{x}_{10}, \mathbf{y}_{10}, \mathbf{z}_{10}$ denote the basis of the 30-dimensional space generated by the displacements of the ten atoms in the x, y and z directions, respectively. If we apply the projection operator $\mathbf{P}_{11}^{(1+)}(\mathbf{0})$ to the basis vector \mathbf{z}_1 , we obtain the first symmetry coordinate according to equation (2.1.3.52):

$$\mathbf{E}(\mathbf{0}, 1^{+11}) = \mathbf{P}_{11}^{(1+)}(\mathbf{0}) \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ 0 \\ \vdots \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix} = \mathbf{P}_{11}^{(1+)}(\mathbf{0}) \mathbf{z}_1 = \mathbf{z}_1.$$

In a similar way we may use the basis vectors $\mathbf{z}_2, \mathbf{x}_3, \mathbf{z}_3$ and \mathbf{x}_5 in order to generate the other symmetry coordinates:

$$\begin{aligned} \mathbf{E}(\mathbf{0}, 1^{+21}) &= \mathbf{P}_{11}^{(1+)}(\mathbf{0}) \mathbf{z}_2 = \mathbf{z}_2 \\ \mathbf{E}(\mathbf{0}, 1^{+31}) &= \mathbf{P}_{11}^{(1+)}(\mathbf{0}) \mathbf{x}_3 \\ &= \frac{1}{8}[\mathbf{x}_3 - \mathbf{x}_4 - \mathbf{y}_5 - \mathbf{y}_6 + \mathbf{x}_7 - \mathbf{x}_8 + \mathbf{y}_9 + \mathbf{y}_{10}] \\ \mathbf{E}(\mathbf{0}, 1^{+41}) &= \mathbf{P}_{11}^{(1+)}(\mathbf{0}) \mathbf{z}_3 \\ &= \frac{1}{8}[\mathbf{z}_3 + \mathbf{z}_4 + \mathbf{z}_5 + \mathbf{z}_6 + \mathbf{z}_7 + \mathbf{z}_8 + \mathbf{z}_9 + \mathbf{z}_{10}] \\ \mathbf{E}(\mathbf{0}, 1^{+51}) &= \mathbf{P}_{11}^{(1+)}(\mathbf{0}) \mathbf{x}_5 \\ &= \frac{1}{8}[-\mathbf{y}_3 + \mathbf{y}_4 + \mathbf{x}_5 - \mathbf{x}_6 + \mathbf{y}_7 - \mathbf{y}_8 + \mathbf{x}_9 - \mathbf{x}_{10}]. \end{aligned}$$

(It can easily be shown that all the other basis vectors would lead to linearly dependent symmetry coordinates.)

Any eigenvector of the dynamical matrix corresponding to the irreducible representation $\tau^{(1+)}$ is necessarily some linear combination of these five symmetry coordinates. Hence it may be concluded that for all lattice vibrations of this symmetry, the displacements of atoms 1 and 2 can only be along the tetragonal axis. Moreover, the displacements of atoms 3 to 10 have to be identical along \mathbf{z} , and pairs of atoms vibrate in opposite directions within the xy plane.

For the representation $\tau^{(1-)}$ we obtain the following symmetry coordinates when $\mathbf{P}_{11}^{(1-)}(\mathbf{0})$ is applied to $\mathbf{x}_3, \mathbf{z}_3$ and \mathbf{x}_5 :

$$\begin{aligned} \mathbf{E}(\mathbf{0}, 1^{-11}) &= \mathbf{P}_{11}^{(1-)}(\mathbf{0}) \mathbf{x}_3 \\ &= \frac{1}{8}[\mathbf{x}_3 - \mathbf{x}_4 + \mathbf{y}_5 - \mathbf{y}_6 - \mathbf{x}_7 + \mathbf{x}_8 + \mathbf{y}_9 - \mathbf{y}_{10}] \\ \mathbf{E}(\mathbf{0}, 1^{-21}) &= \mathbf{P}_{11}^{(1-)}(\mathbf{0}) \mathbf{z}_3 \\ &= \frac{1}{8}[\mathbf{z}_3 + \mathbf{z}_4 - \mathbf{z}_5 + \mathbf{z}_6 - \mathbf{z}_7 - \mathbf{z}_8 + \mathbf{z}_9 - \mathbf{z}_{10}] \\ \mathbf{E}(\mathbf{0}, 1^{-31}) &= \mathbf{P}_{11}^{(1-)}(\mathbf{0}) \mathbf{x}_5 \\ &= \frac{1}{8}[\mathbf{y}_3 - \mathbf{y}_4 + \mathbf{x}_5 + \mathbf{x}_6 + \mathbf{y}_7 - \mathbf{y}_8 - \mathbf{x}_9 - \mathbf{x}_{10}]. \end{aligned}$$

Obviously, none of the corresponding phonons exhibits any displacement of atoms 1 and 2. There is an antiphase motion of pairs of atoms not only within the tetragonal plane but also along the tetragonal z axis.

For the representations $\tau^{(3\pm)}$ we obtain the following projection operators:

$$\mathbf{P}_{11}^{(3\pm)}(\mathbf{0}) = \frac{1}{8} \begin{pmatrix} \Sigma_3^\pm & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \Sigma_3^\pm & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \mathbf{E} & \mathbf{D}_{180}^\pm & \mp \mathbf{m}_{[110]} & -\mathbf{D}_{90}^\pm & \pm \mathbf{m}_y & \pm \mathbf{m}_x & -\mathbf{D}_{270}^\pm & \mp \mathbf{m}_{[110]} \\ 0 & 0 & \mathbf{D}_{180}^\pm & \mathbf{E} & \mp \mathbf{m}_{[110]} & -\mathbf{D}_{270}^\pm & \pm \mathbf{m}_x & \pm \mathbf{m}_y & -\mathbf{D}_{90}^\pm & \mp \mathbf{m}_{[110]} \\ 0 & 0 & \mp \mathbf{m}_{[110]} & \mp \mathbf{m}_{[110]} & \mathbf{E} & \pm \mathbf{m}_x & -\mathbf{D}_{270}^\pm & -\mathbf{D}_{90}^\pm & \pm \mathbf{m}_y & \mathbf{D}_{180}^\pm \\ 0 & 0 & -\mathbf{D}_{270}^\pm & -\mathbf{D}_{90}^\pm & \pm \mathbf{m}_x & \mathbf{E} & \mp \mathbf{m}_{[110]} & \mp \mathbf{m}_{[110]} & \mathbf{D}_{180}^\pm & \pm \mathbf{m}_y \\ 0 & 0 & \pm \mathbf{m}_y & \pm \mathbf{m}_x & -\mathbf{D}_{90}^\pm & \mp \mathbf{m}_{[110]} & \mathbf{E} & \mathbf{D}_{180}^\pm & \mp \mathbf{m}_{[110]} & -\mathbf{D}_{270}^\pm \\ 0 & 0 & \pm \mathbf{m}_x & \pm \mathbf{m}_y & -\mathbf{D}_{270}^\pm & \mp \mathbf{m}_{[110]} & \mathbf{D}_{180}^\pm & \mathbf{E} & \mp \mathbf{m}_{[110]} & -\mathbf{D}_{90}^\pm \\ 0 & 0 & -\mathbf{D}_{90}^\pm & -\mathbf{D}_{270}^\pm & \pm \mathbf{m}_y & \mathbf{D}_{180}^\pm & \mp \mathbf{m}_{[110]} & \mp \mathbf{m}_{[110]} & \mathbf{E} & \pm \mathbf{m}_x \\ 0 & 0 & \mp \mathbf{m}_{[110]} & \mp \mathbf{m}_{[110]} & \mathbf{D}_{180}^\pm & \pm \mathbf{m}_y & -\mathbf{D}_{90}^\pm & -\mathbf{D}_{270}^\pm & \pm \mathbf{m}_x & \mathbf{E} \end{pmatrix}$$

with

$$\Sigma_3^\pm = \mathbf{E} - \mathbf{D}_{90}^\pm + \mathbf{D}_{180}^\pm - \mathbf{D}_{270}^\pm \pm \mathbf{m}_x \pm \mathbf{m}_y \mp \mathbf{m}_{[110]} \mp \mathbf{m}_{[110]} = \mathbf{0}.$$

Both representations appear three times in the decomposition of the \mathbf{T} representation. Hence, we expect three phonons of each symmetry and also three linearly independent symmetry coordinates. These are generated if the projection operators are applied to the basis vectors $\mathbf{x}_3, \mathbf{z}_3$ and \mathbf{x}_5 :

$$\begin{aligned} \mathbf{E}(\mathbf{0}, 3^\pm 11) &= \mathbf{P}_{11}^{(3^\pm)}(\mathbf{0}) \mathbf{x}_3 \\ &= \frac{1}{8}[\mathbf{x}_3 - \mathbf{x}_4 \pm \mathbf{y}_5 + \mathbf{y}_6 \pm \mathbf{x}_7 \mp \mathbf{x}_8 - \mathbf{y}_9 \mp \mathbf{y}_{10}] \\ \mathbf{E}(\mathbf{0}, 3^\pm 21) &= \mathbf{P}_{11}^{(3^\pm)}(\mathbf{0}) \mathbf{z}_3 \\ &= \frac{1}{8}[\mathbf{z}_3 + \mathbf{z}_4 \mp \mathbf{z}_5 - \mathbf{z}_6 \pm \mathbf{z}_7 \pm \mathbf{z}_8 - \mathbf{z}_9 \mp \mathbf{z}_{10}] \\ \mathbf{E}(\mathbf{0}, 3^\pm 11) &= \mathbf{P}_{11}^{(3^\pm)}(\mathbf{0}) \mathbf{x}_5 \\ &= \frac{1}{8}[\pm \mathbf{y}_3 \mp \mathbf{y}_4 + \mathbf{x}_5 \mp \mathbf{x}_6 - \mathbf{y}_7 + \mathbf{y}_8 \pm \mathbf{x}_9 - \mathbf{x}_{10}]. \end{aligned}$$

Just as for representation $\tau^{(1-)}$, the symmetry coordinates corresponding to representations $\tau^{(3^\pm)}$ do not contain any component of atoms 1 and 2. Consequently, all lattice modes of these symmetries leave the atoms on the fourfold axis at their equilibrium positions at rest.

Representation $\tau^{(2)}$ is two-dimensional and appears eight times in the decomposition of the \mathbf{T} representation. Hence, there are 16 doubly degenerate phonons of this symmetry. According to (2.1.3.51), four projection operators $\mathbf{P}_{11}^{(2)}(\mathbf{0}), \mathbf{P}_{21}^{(2)}(\mathbf{0}), \mathbf{P}_{12}^{(2)}(\mathbf{0})$ and $\mathbf{P}_{22}^{(2)}(\mathbf{0})$ can in principle be constructed, the latter two being, however, equivalent to the former ones:

$$\mathbf{P}_{11}^{(2)}(\mathbf{0}) = \frac{1}{4} \begin{pmatrix} \Sigma_2^\pm & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \Sigma_2^\pm & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \mathbf{E} & -\mathbf{D}_{180}^\pm & 0 & \pm i\mathbf{D}_{90}^\pm & 0 & 0 & \mp i\mathbf{D}_{270}^\pm & 0 \\ 0 & 0 & -\mathbf{D}_{180}^\pm & \mathbf{E} & 0 & \mp i\mathbf{D}_{270}^\pm & 0 & 0 & \pm i\mathbf{D}_{90}^\pm & 0 \\ 0 & 0 & 0 & 0 & \mathbf{E} & 0 & \mp i\mathbf{D}_{270}^\pm & \pm i\mathbf{D}_{90}^\pm & 0 & -\mathbf{D}_{180}^\pm \\ 0 & 0 & \mp i\mathbf{D}_{270}^\pm & \pm i\mathbf{D}_{90}^\pm & 0 & \mathbf{E} & 0 & 0 & -\mathbf{D}_{180}^\pm & 0 \\ 0 & 0 & 0 & 0 & \pm i\mathbf{D}_{90}^\pm & 0 & \mathbf{E} & -\mathbf{D}_{180}^\pm & 0 & \mp i\mathbf{D}_{270}^\pm \\ 0 & 0 & 0 & 0 & \mp i\mathbf{D}_{270}^\pm & 0 & -\mathbf{D}_{180}^\pm & \mathbf{E} & 0 & \pm i\mathbf{D}_{90}^\pm \\ 0 & 0 & \pm i\mathbf{D}_{90}^\pm & \mp i\mathbf{D}_{270}^\pm & 0 & -\mathbf{D}_{180}^\pm & 0 & 0 & \mathbf{E} & 0 \\ 0 & 0 & 0 & 0 & -\mathbf{D}_{180}^\pm & 0 & \pm i\mathbf{D}_{90}^\pm & \mp i\mathbf{D}_{270}^\pm & 0 & \mathbf{E} \end{pmatrix}$$

and

$$\mathbf{P}_{21}^{(2)}(\mathbf{0}) = \frac{1}{4} \begin{pmatrix} \Delta_2^\pm & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \Delta_2^\pm & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \pm i\mathbf{m}_{[110]} & 0 & -\mathbf{m}_y & \mathbf{m}_x & 0 & \mp i\mathbf{m}_{[110]} \\ 0 & 0 & 0 & 0 & \mp i\mathbf{m}_{[110]} & 0 & \mathbf{m}_x & -\mathbf{m}_y & 0 & \pm i\mathbf{m}_{[110]} \\ 0 & 0 & \pm i\mathbf{m}_{[110]} & \mp i\mathbf{m}_{[110]} & 0 & \mathbf{m}_x & 0 & 0 & -\mathbf{m}_y & 0 \\ 0 & 0 & 0 & 0 & \mathbf{m}_x & 0 & \pm i\mathbf{m}_{[110]} & \mp i\mathbf{m}_{[110]} & 0 & -\mathbf{m}_y \\ 0 & 0 & -\mathbf{m}_y & \mathbf{m}_x & 0 & \pm i\mathbf{m}_{[110]} & 0 & 0 & \mp i\mathbf{m}_{[110]} & 0 \\ 0 & 0 & \mathbf{m}_x & -\mathbf{m}_y & 0 & \mp i\mathbf{m}_{[110]} & 0 & 0 & \pm i\mathbf{m}_{[110]} & 0 \\ 0 & 0 & 0 & 0 & -\mathbf{m}_y & 0 & \mp i\mathbf{m}_{[110]} & \pm i\mathbf{m}_{[110]} & 0 & \mathbf{m}_x \\ 0 & 0 & \mp i\mathbf{m}_{[110]} & \pm i\mathbf{m}_{[110]} & 0 & -\mathbf{m}_y & 0 & 0 & \mathbf{m}_x & 0 \end{pmatrix}$$

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with

$$\Sigma_2^\pm = \mathbf{E} \pm i\mathbf{D}_{90}^z - \mathbf{D}_{180}^z \mp i\mathbf{D}_{270}^z = \begin{pmatrix} 2 & \mp 2i & 0 \\ \pm 2i & 2 & 0 \\ 0 & 0 & 0 \end{pmatrix},$$

$$\Lambda_2^\pm = \mathbf{m}_x - \mathbf{m}_y \pm i\mathbf{m}_{[110]} \mp i\mathbf{m}_{[\bar{1}\bar{1}0]} = \begin{pmatrix} -2 & \mp 2i & 0 \\ \mp 2i & 2 & 0 \\ 0 & 0 & 0 \end{pmatrix}.$$

The projection operator $\mathbf{P}_{11}^{(2)}(\mathbf{0})$ applied to the basis vectors $\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \mathbf{x}_5, \mathbf{x}_6, \mathbf{x}_7, \mathbf{z}_3$ and \mathbf{z}_5 yields eight symmetry coordinates for eight phonon modes with different eigenfrequencies. Owing to the degeneracy, each of these phonons has a counterpart with the same frequency but with a different linearly independent eigenvector. These new eigenvectors are built from another set of symmetry coordinates, which is generated if the other operator $\mathbf{P}_{21}^{(2)}(\mathbf{0})$ is applied to the same vectors $\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \mathbf{x}_5, \mathbf{x}_6, \mathbf{x}_7, \mathbf{z}_3$ and \mathbf{z}_5 . The two sets of symmetry coordinates are

$$\begin{aligned} \mathbf{E}(\mathbf{0}, 211) &= \mathbf{P}_{11}^{(2)}(\mathbf{0}) \mathbf{x}_1 = \frac{1}{2}[\mathbf{x}_1 + i\mathbf{y}_1] \\ \mathbf{E}(\mathbf{0}, 221) &= \mathbf{P}_{11}^{(2)}(\mathbf{0}) \mathbf{x}_2 = \frac{1}{2}[\mathbf{x}_2 + i\mathbf{y}_2] \\ \mathbf{E}(\mathbf{0}, 231) &= \mathbf{P}_{11}^{(2)}(\mathbf{0}) \mathbf{x}_3 = \frac{1}{4}[\mathbf{x}_3 + \mathbf{x}_4 + i\mathbf{y}_6 + i\mathbf{y}_9] \\ \mathbf{E}(\mathbf{0}, 241) &= \mathbf{P}_{11}^{(2)}(\mathbf{0}) \mathbf{x}_5 = \frac{1}{4}[\mathbf{x}_5 + \mathbf{x}_{10} + i\mathbf{y}_7 + i\mathbf{y}_8] \\ \mathbf{E}(\mathbf{0}, 251) &= \mathbf{P}_{11}^{(2)}(\mathbf{0}) \mathbf{x}_6 = \frac{1}{4}[\mathbf{x}_6 + \mathbf{x}_9 + i\mathbf{y}_3 + i\mathbf{y}_4] \\ \mathbf{E}(\mathbf{0}, 261) &= \mathbf{P}_{11}^{(2)}(\mathbf{0}) \mathbf{x}_7 = \frac{1}{4}[\mathbf{x}_7 + \mathbf{x}_8 + i\mathbf{y}_5 + i\mathbf{y}_{10}] \\ \mathbf{E}(\mathbf{0}, 271) &= \mathbf{P}_{11}^{(2)}(\mathbf{0}) \mathbf{z}_3 = \frac{1}{4}[\mathbf{z}_3 - \mathbf{z}_4 - i\mathbf{z}_6 + i\mathbf{z}_9] \\ \mathbf{E}(\mathbf{0}, 281) &= \mathbf{P}_{11}^{(2)}(\mathbf{0}) \mathbf{z}_5 = \frac{1}{4}[\mathbf{z}_5 - \mathbf{z}_{10} + i\mathbf{z}_7 - i\mathbf{z}_8] \\ \\ \mathbf{E}(\mathbf{0}, 212) &= \mathbf{P}_{21}^{(2)}(\mathbf{0}) \mathbf{x}_1 = \frac{1}{2}[-\mathbf{x}_1 + i\mathbf{y}_1] \\ \mathbf{E}(\mathbf{0}, 222) &= \mathbf{P}_{21}^{(2)}(\mathbf{0}) \mathbf{x}_2 = \frac{1}{2}[-\mathbf{x}_2 + i\mathbf{y}_2] \\ \mathbf{E}(\mathbf{0}, 232) &= \mathbf{P}_{21}^{(2)}(\mathbf{0}) \mathbf{x}_3 = \frac{1}{4}[-\mathbf{x}_7 - \mathbf{x}_8 + i\mathbf{y}_5 + i\mathbf{y}_{10}] \\ \mathbf{E}(\mathbf{0}, 242) &= \mathbf{P}_{21}^{(2)}(\mathbf{0}) \mathbf{x}_5 = \frac{1}{4}[-\mathbf{x}_6 - \mathbf{x}_9 + i\mathbf{y}_3 + i\mathbf{y}_4] \\ \mathbf{E}(\mathbf{0}, 252) &= \mathbf{P}_{21}^{(2)}(\mathbf{0}) \mathbf{x}_6 = \frac{1}{4}[-\mathbf{x}_5 - \mathbf{x}_{10} + i\mathbf{y}_7 + i\mathbf{y}_8] \\ \mathbf{E}(\mathbf{0}, 262) &= \mathbf{P}_{21}^{(2)}(\mathbf{0}) \mathbf{x}_7 = \frac{1}{4}[-\mathbf{x}_3 - \mathbf{x}_4 + i\mathbf{y}_6 + i\mathbf{y}_9] \\ \mathbf{E}(\mathbf{0}, 272) &= \mathbf{P}_{21}^{(2)}(\mathbf{0}) \mathbf{z}_3 = \frac{1}{4}[-\mathbf{z}_7 + \mathbf{z}_8 - i\mathbf{z}_5 + i\mathbf{z}_{10}] \\ \mathbf{E}(\mathbf{0}, 282) &= \mathbf{P}_{21}^{(2)}(\mathbf{0}) \mathbf{z}_5 = \frac{1}{4}[\mathbf{z}_6 - \mathbf{z}_9 - i\mathbf{z}_3 + i\mathbf{z}_4]. \end{aligned}$$

Looking carefully at these sets of symmetry coordinates, one recognises that both vector spaces are spanned by mutually complex conjugate symmetry coordinates.

Collecting all symmetry coordinates as column vectors within a 30×30 matrix we finally obtain the matrix shown in Fig. 2.1.3.7. For simplicity, only nonzero elements are displayed. This matrix can be used for the block-diagonalization of any dynamical matrix that describes the dynamical behaviour of our model crystal.

2.1.3.5. Degeneracy of lattice vibrations

Whenever two phonon modes of the same wavevector exhibit identical frequencies but linearly independent eigenvectors, these modes are called *degenerate*. As discussed in the preceding sections, the symmetry of the crystal lattice may cause degeneracies if there are higher-dimensional irreducible representations of the point group of the phonon wavevector. Two-dimensional representations yield twofold degenerate lattice vibrations, whereas threefold degeneracy may be found for special wavevectors in cubic crystals exhibiting three-dimensional irreducible representations. In addition, there are two other reasons for the possible existence of degenerate lattice vibra-

tions: *accidental degeneracy* and degeneracy due to *time-reversal invariance* of the lattice vibrations. Both phenomena will be described in the following.

2.1.3.5.1. Accidental degeneracy

The symmetry analysis of lattice vibrations provides a powerful tool not only for the characterization of eigenvectors but also for the presentation of experimental results. In neutron scattering experiments, for example, a series of single phonons may be detected but symmetry determines which of these phonons belong to the same branch, *i.e.* how the single phonons have to be connected by a dispersion curve. The decision as to which of Figs. 2.1.3.8(a) or (b), which represent the same experimental results as full circles, is the correct one can be made by symmetry arguments only. In Fig. 2.1.3.8(a) the two phonon branches intersect. Thus, there are two degenerate phonons at the single wavevector \mathbf{q}^* . From the symmetry point of view, this particular wavevector has no special properties, *i.e.* the point group $G_o(\mathbf{q}^*)$ is just the same as for neighbouring wavevectors. Hence, the degeneracy cannot be due to symmetry and the respective eigenvectors \mathbf{e}_1 and \mathbf{e}_2 are not related by any transformation matrix. As a consequence, the two phonons cannot belong to the same irreducible representation, because otherwise every linear combination $\alpha\mathbf{e}_1 + \beta\mathbf{e}_2$ would equally well represent a valid eigenvector to the same eigenvalue with the same symmetry. It is, however, highly improbable that the special nature of the interatomic interactions gives rise to this uncertainty of eigenvectors at some wavevector within the Brillouin zone. Rather, it is expected that any infinitesimal change of force constants will favour one particular linear combination which, consequently, must correspond to a phonon of lower frequency. At the same time, there will be another well defined orthogonal eigenvector with slightly higher frequency – just as is represented in Fig. 2.1.3.8(b). Hence, two phonon branches of the same symmetry do not intersect and yield a frequency gap. This phenomenon is sometimes called *anticrossing* behaviour. It is associated with an eigenvector exchange between the two branches.

Accidental degeneracy according to Fig. 2.1.3.8(a), on the other hand, can only be observed if the two phonon branches belong to different irreducible representations. In this case, the eigenvectors are uniquely determined even at \mathbf{q}^* since a mixing is forbidden by symmetry.

2.1.3.5.2. Time-reversal degeneracy

In Section 2.1.3.3, we considered in some detail the symmetry of phonon eigenvectors with respect to the symmetry operations contained in the point group $G_o(\mathbf{q})$ of the wavevector. We know, however, that those symmetry operations that invert the wavevector give rise to additional constraints for the dynamical matrix. A lattice vibration with wavevector $-\mathbf{q}$ can also be regarded as a wave travelling in the opposite direction $+\mathbf{q}$ on a reversed timescale. Since the classical equations of motion are invariant with respect to time reversal, both phonon eigenvectors, $\mathbf{e}(\mathbf{q})$ and $\mathbf{e}(-\mathbf{q})$, are related and additional degeneracies may appear if there are symmetry operations that transform \mathbf{q} into $-\mathbf{q}$.

Let \mathbf{A} be the rotational part of such a symmetry operation. We have shown in Section 2.1.3.1 that anti-unitary matrix operators $\mathbf{T}(\mathbf{q}, \mathbf{A})$ can be defined that commute with the dynamical matrix. Not only the eigenvectors $\mathbf{e}(\mathbf{q}, s\lambda)$, $\lambda = 1, \dots, f_s$, but also

$$\bar{\mathbf{e}}(\mathbf{q}, s\lambda) = \mathbf{T}(\mathbf{q}, \mathbf{A}) \mathbf{e}(\mathbf{q}, s\lambda) \quad (2.1.3.59)$$

are therefore eigenvectors corresponding to the same eigenfrequency. If the latter are linear combinations of the former ones, no new information about degeneracies can be expected. If, on the other hand, $\mathbf{T}(\mathbf{q}, \mathbf{A}) \mathbf{e}(\mathbf{q}, s\lambda)$ is orthogonal to all vectors $\mathbf{e}(\mathbf{q}, s'\lambda')$, it belongs to another vector space corresponding to different indices s' and λ' . In this case, the eigenfrequencies $\omega_{\mathbf{q},s\lambda}$

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$\tau^{(1+)}$	$\tau^{(1-)}$	$\tau^{(3+)}$	$\tau^{(3-)}$	$\tau^{(2)}$	
1				1 i	1 -i
1				1 i	1 -i
1	1 -1	1 1	1 1	1 i	-1 i
1	1	1 -1	1 -1	1 i	-1 i
1	1	1	1	1 i	-1 i
1	-1	1 -1	1 -1	i 1	-1 i
1	1	1	1	i -i	-1 i
1	1	1 -1	1 -1	i 1	-1 i
1	-1	1 -1	1 -1	i -i	-1 i
1	1	1	1	i i	-1 i
1	-1	1 -1	1 -1	i -i	-1 i
1	1	1	1	i i	-1 i

Fig. 2.1.3.7. Matrix of symmetry coordinates at $\mathbf{q} = \mathbf{0}$ for the example structure given in Fig. 2.1.3.4 and Table 2.1.3.1.

and $\omega_{\mathbf{q},s'}$ have to be identical and additional degeneracies appear that may even relate different irreducible representations s and s' .

In order to distinguish between the two possibilities, we have to consider the transformation behaviour of the vector $\bar{\mathbf{e}}(\mathbf{q}, sa\lambda)$. According to the multiplication rule for the \mathbf{T} -matrix operators, (2.1.3.32), we obtain

$$\begin{aligned} \mathbf{T}(\mathbf{q}, \mathbf{R}) \bar{\mathbf{e}}(\mathbf{q}, sa\lambda) &= \mathbf{T}(\mathbf{q}, \mathbf{R}) \mathbf{T}(\mathbf{q}, \mathbf{A}) \mathbf{e}(\mathbf{q}, sa\lambda) \\ &= \varphi^*(\mathbf{q}, \mathbf{A}, \mathbf{A}^{-1} \circ \mathbf{R} \circ \mathbf{A}) \varphi(\mathbf{q}, \mathbf{R}, \mathbf{A}) \\ &\quad \times \mathbf{T}(\mathbf{q}, \mathbf{A}) \mathbf{T}(\mathbf{q}, \mathbf{A}^{-1} \circ \mathbf{R} \circ \mathbf{A}) \mathbf{e}(\mathbf{q}, sa\lambda). \end{aligned} \quad (2.1.3.60)$$

The operation $\mathbf{A}^{-1} \circ \mathbf{R} \circ \mathbf{A}$ leaves the wavevector invariant and is therefore an element of the point group $G_o(\mathbf{q})$. Hence the right-hand side can be expressed in terms of the irreducible representation $\tau^{(s)}(\mathbf{q}, \mathbf{R})$:

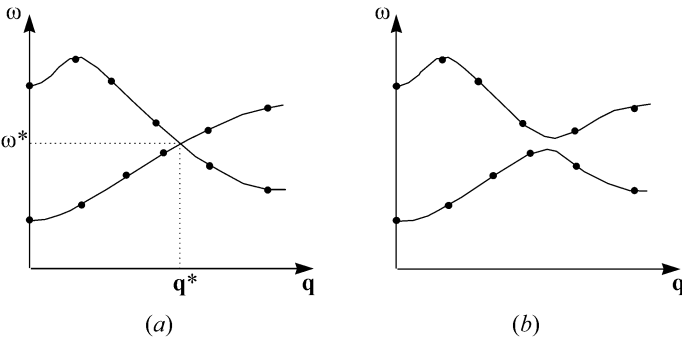


Fig. 2.1.3.8. (a) Accidental degeneracy of phonons with different symmetry. (b) Anticrossing of phonons with the same symmetry (no degeneracy).

$$\begin{aligned} \mathbf{T}(\mathbf{q}, \mathbf{R}) \bar{\mathbf{e}}(\mathbf{q}, sa\lambda) &= \varphi^*(\mathbf{q}, \mathbf{A}, \mathbf{A}^{-1} \circ \mathbf{R} \circ \mathbf{A}) \varphi(\mathbf{q}, \mathbf{R}, \mathbf{A}) \mathbf{T}(\mathbf{q}, \mathbf{A}) \\ &\quad \times \sum_{\lambda'=1}^{f_s} \tau_{\lambda'\lambda}^{(s)}(\mathbf{q}, \mathbf{A}^{-1} \circ \mathbf{R} \circ \mathbf{A}) \mathbf{e}(\mathbf{q}, sa\lambda') \\ &= \varphi^*(\mathbf{q}, \mathbf{A}, \mathbf{A}^{-1} \circ \mathbf{R}) \varphi^*(\mathbf{q}, \mathbf{A}^{-1} \circ \mathbf{R}, \mathbf{A}) \\ &\quad \times \sum_{\lambda'=1}^{f_s} \tau_{\lambda'\lambda}^{(s)*}(\mathbf{q}, \mathbf{A}^{-1} \circ \mathbf{R} \circ \mathbf{A}) \bar{\mathbf{e}}(\mathbf{q}, sa\lambda'). \end{aligned} \quad (2.1.3.61)$$

Obviously, the new eigenvectors $\bar{\mathbf{e}}(\mathbf{q}, sa\lambda)$ transform according to the conjugated representation $\bar{\tau}^{(s)}(\mathbf{q}, \mathbf{R})$ defined by

$$\begin{aligned} \bar{\tau}^{(s)}(\mathbf{q}, \mathbf{R}) &= \varphi^*(\mathbf{q}, \mathbf{A}, \mathbf{A}^{-1} \circ \mathbf{R}) \varphi^*(\mathbf{q}, \mathbf{A}^{-1} \circ \mathbf{R}, \mathbf{A}) \\ &\quad \times \tau^{(s)*}(\mathbf{q}, \mathbf{A}^{-1} \circ \mathbf{R} \circ \mathbf{A}), \end{aligned} \quad (2.1.3.62)$$

\mathbf{A} being an arbitrary representative of those symmetry operations that invert the wavevector \mathbf{q} .

If the irreducible representations $\bar{\tau}^{(s)}(\mathbf{q}, \mathbf{R})$ and $\tau^{(s)}(\mathbf{q}, \mathbf{R})$ are not equivalent, the eigenvectors $\bar{\mathbf{e}}(\mathbf{q}, sa\lambda)$ and $\mathbf{e}(\mathbf{q}, sa\lambda')$ are linearly independent and, hence, the vibrations of the two representations are degenerate. In this case, $\tau^{(s)}(\mathbf{q}, \mathbf{R})$ is called a representation of the third kind. Within the decomposition of the \mathbf{T} representation, $\tau^{(s)}(\mathbf{q}, \mathbf{R})$ and $\bar{\tau}^{(s)}(\mathbf{q}, \mathbf{R})$ always appear in pairs.

If, on the other hand, the two representations are equivalent, there is a matrix β with

$$\bar{\tau}^{(s)}(\mathbf{q}, \mathbf{R}) = \beta^{-1} \tau^{(s)}(\mathbf{q}, \mathbf{R}) \beta \quad (2.1.3.63)$$

corresponding to a transformation of the coordinate system. It can be shown that the product $\beta \beta^*$ has the following form:

$$\beta \beta^* = \pm \varphi(\mathbf{q}, \mathbf{A}, \mathbf{A}) \tau^{(s)}(\mathbf{q}, \mathbf{A}^2). \quad (2.1.3.64)$$

In many cases, \mathbf{A} is of order 2, i.e. $\mathbf{A}^2 = \mathbf{E}$ (for $\mathbf{A} = \mathbf{i}$ or $\mathbf{A} = \mathbf{m}$, for example), and the right-hand side of (2.1.3.64) reduces to $\pm \mathbf{E}$.

Those representations for which the + sign in (2.1.3.64) holds have come to be called *representations of the first kind* [$\beta \beta^* = +\varphi(\mathbf{q}, \mathbf{A}, \mathbf{A}) \tau^{(s)}(\mathbf{q}, \mathbf{A}^2)$] and those that correspond to the - sign

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representations of the second kind [$\boldsymbol{\beta}\boldsymbol{\beta}^* = -\varphi(\mathbf{q}, \mathbf{A}, \mathbf{A})\boldsymbol{\tau}^{(s)}(\mathbf{q}, \mathbf{A}^2)$]. Without going into the details of the two cases, we merely wish to present the results that are most relevant for our discussion. For a more detailed presentation see *e.g.* Maradudin & Vosko (1968).

For representations of the first kind, the eigenvectors $\bar{\mathbf{e}}(\mathbf{q}, sa\lambda)$ and $\mathbf{e}(\mathbf{q}, sa\lambda')$ are related by a linear transformation. Hence there are no additional degeneracies due to the time-reversal invariance of the equation of motion. Let us consider the special case of a point group $G_o(\mathbf{q})$ whose elements commute with the symmetry operation \mathbf{A} . Crystals with a centre of inversion always meet this condition. For wavevectors within the Brillouin zone or for symmorphic space groups all multipliers are unity and $\bar{\boldsymbol{\tau}}^{(s)}(\mathbf{q}, \mathbf{R}) = \boldsymbol{\tau}^{(s)*}(\mathbf{q}, \mathbf{R})$. In this case, representations are of the first kind if they are real representations.

For representations of the second kind, $\bar{\mathbf{e}}(\mathbf{q}, sa\lambda)$ and $\mathbf{e}(\mathbf{q}, sa\lambda')$ are linearly independent. The corresponding lattice vibrations are degenerate due to time-reversal invariance. Consequently, the multiplicity of the representation $\boldsymbol{\tau}^{(s)}(\mathbf{q}, \mathbf{R})$ in the decomposition of the \mathbf{T} representation is an even number and pairs of eigenfrequencies are identical:

$$\omega_{\mathbf{q},sa} = \omega_{\mathbf{q},sa'} \quad \text{with } a \neq a'. \quad (2.1.3.65)$$

The theory of characters provides us with a rather simple criterion for the distinction between representations of the first, second or third kind. Without any proof, we simply present the result that is particularly important for practical work:

$$(1/|G|) \sum_{\mathbf{R}} \varphi(\mathbf{q}, \mathbf{A} \circ \mathbf{R}, \mathbf{A} \circ \mathbf{R}) \chi_{\boldsymbol{\tau}^{(s)}}(\mathbf{q}, (\mathbf{A} \circ \mathbf{R})^2) \\ = \left\{ \begin{array}{l} +1 \text{ for representations of the first kind} \\ -1 \text{ for representations of the second kind} \\ 0 \text{ for representations of the third kind} \end{array} \right\}. \quad (2.1.3.66)$$

Finally, let us consider the special case of a real dynamical matrix. This can be found for crystals in which each atom is a centre of inversion or for special wavevectors on the Brillouin-zone boundary or at the Γ point, for example. In this case, the dynamical matrix commutes with the operator \mathbf{K}_o that transforms arbitrary vectors into their complex-conjugate counterparts. Hence, the vectors $\mathbf{K}_o \mathbf{e}(\mathbf{q}, sa\lambda) = \mathbf{e}^*(\mathbf{q}, sa\lambda)$ are eigenvectors to the eigenvalue $\omega_{\mathbf{q},sa}^2$ as well as $\mathbf{e}(\mathbf{q}, sa\lambda)$ itself. Since $\mathbf{e}(\mathbf{q}, sa\lambda)$ transforms under the elements of the point group $G_o(\mathbf{q})$ according to the irreducible representation $\boldsymbol{\tau}^{(s)}(\mathbf{q})$, $\mathbf{e}^*(\mathbf{q}, sa\lambda)$ belongs to the complex-conjugate representation. If the two representations are not real ones and therefore not identical, the corresponding lattice vibrations have to be degenerate. Every linear combination of the eigenvectors $\mathbf{e}(\mathbf{q}, sa\lambda)$ and $\mathbf{e}^*(\mathbf{q}, sa\lambda)$ is an eigenvector as well. Thus, we are free to choose real eigenvectors, namely: $(1/\sqrt{2})[\mathbf{e}(\mathbf{q}, sa\lambda) + \mathbf{e}^*(\mathbf{q}, sa\lambda)]$ and $(1/\sqrt{2}i)[\mathbf{e}(\mathbf{q}, sa\lambda) - \mathbf{e}^*(\mathbf{q}, sa\lambda)]$.

2.1.3.5.3. Example

Let us consider the space group $P\bar{6}$. For wavevectors along the hexagonal axis, the point group $G_o(\mathbf{q})$ consists of the three symmetry operations E , D_{120}^z and D_{240}^z . Being a cyclic group, its irreducible representations are one-dimensional (see Table 2.1.3.4). The mirror plane m_z inverts the wavevector and the two threefold rotations are self-conjugated with respect to m_z :

$$\mathbf{m}_z D_{120}^z \mathbf{m}_z = D_{120}^z \\ \mathbf{m}_z D_{240}^z \mathbf{m}_z = D_{240}^z.$$

If we remember that for symmorphic space groups all multipliers are unity, we obtain the following conjugate representations according to (2.1.3.62):

$$\bar{\boldsymbol{\tau}}^{(1)} = \boldsymbol{\tau}^{(1)*} = \boldsymbol{\tau}^{(1)} \\ \bar{\boldsymbol{\tau}}^{(2)} = \boldsymbol{\tau}^{(2)*} = \boldsymbol{\tau}^{(3)} \\ \bar{\boldsymbol{\tau}}^{(3)} = \boldsymbol{\tau}^{(3)*} = \boldsymbol{\tau}^{(2)}.$$

Obviously, $\bar{\boldsymbol{\tau}}^{(2)}$ and $\boldsymbol{\tau}^{(2)}$ are inequivalent and, hence, pairs of phonons corresponding to representations $\boldsymbol{\tau}^{(2)}$ and $\boldsymbol{\tau}^{(3)}$, respectively, are degenerate. The two transverse acoustic phonon branches in particular not only leave the Γ point with the same slope as determined by the elastic stiffness $c_{44} = c_{2323}$ (*cf.* Section 2.1.2.4 and Chapter 1.3) but are strictly identical throughout the whole Brillouin zone.

Another example may illustrate the degeneracy of phonons at special wavevectors where the elements of the dynamical matrix are real quantities. Let us consider the nonsymmorphic space group $P6_3$. For the Γ point ($\mathbf{q} = \mathbf{0}$), the one-dimensional representations of this cyclic group are collected in Table 2.1.3.5. Obviously, $\boldsymbol{\tau}^{(2)}(\mathbf{0})$ and $\boldsymbol{\tau}^{(6)}(\mathbf{0})$ form a pair of complex-conjugated representations as well as $\boldsymbol{\tau}^{(3)}(\mathbf{0})$ and $\boldsymbol{\tau}^{(5)}(\mathbf{0})$. Therefore, always two lattice vibrations of these symmetries exhibit the same frequencies. The eigenvectors for representation $\boldsymbol{\tau}^{(6)}(\mathbf{0})$ or $\boldsymbol{\tau}^{(5)}(\mathbf{0})$ can be combined with the eigenvectors of corresponding modes of representations $\boldsymbol{\tau}^{(2)}(\mathbf{0})$ or $\boldsymbol{\tau}^{(3)}(\mathbf{0})$, respectively, to yield real quantities.

For wavevectors within the Brillouin zone along the hexagonal axis, the irreducible representations are the same as for the Γ point. However, the elements of the dynamical matrix are complex and symmetry does not yield any degeneracies. Hence phonons can be distinguished according to the six different representations.

At the Brillouin-zone boundary along the hexagonal axis ($\mathbf{q} = \mathbf{c}^*/2$, the A point), one has to take into account multipliers of the form $\exp[i\mathbf{q}\mathbf{v}(\mathbf{R})]$ since the space group is nonsymmorphic. For symmetry operations without fractional translation (E , D_{120}^z , D_{240}^z) this factor is unity, whereas it equals the complex unit i for the other elements of the point group (D_{60}^z , D_{180}^z , D_{300}^z). Hence the six irreducible multiplier representations are as shown in Table 2.1.3.6. Now we have three pairs of complex-conjugate representations, namely: $\boldsymbol{\tau}^{(1)}(\mathbf{c}^*/2)$ and $\boldsymbol{\tau}^{(4)}(\mathbf{c}^*/2)$; $\boldsymbol{\tau}^{(2)}(\mathbf{c}^*/2)$ and $\boldsymbol{\tau}^{(3)}(\mathbf{c}^*/2)$; and $\boldsymbol{\tau}^{(5)}(\mathbf{c}^*/2)$ and $\boldsymbol{\tau}^{(6)}(\mathbf{c}^*/2)$. Again, pairs of phonons of corresponding representations are degenerate. As a consequence, the phonon dispersion curves need not approach the Brillouin-zone boundary with a horizontal slope but meet another branch with the opposite slope.

In conclusion, group-theoretical considerations for wavevectors along the hexagonal axis yield at the centre (Γ point) as well as at the boundary (A point) of the first Brillouin zone pairs of degenerate phonon modes. Both modes belong to complex-conjugate representations. This result can be used in order to display the dispersion curves very clearly in an *extended zone scheme* plotting the phonon branches of different symmetries alternately from Γ to A and from A back to Γ as illustrated in Fig. 2.1.3.9. Here, the phonon dispersion for the room-temperature phase of KLiSO_4 is shown as an example. Note that irreducible representations are frequently denoted by the letters A, B, E, T instead of our notation $\boldsymbol{\tau}^{(i)}$. T and E are reserved for representations that (at the Γ point) are triply and doubly degenerate, respectively. An index \pm or *g/u* is often used to distinguish representations that are symmetric (*gerade*) and antisymmetric (*ungerade*) with respect to a prominent symmetry operation, *e.g.* a centre of inversion or, in the case of $P6_3$, the twofold axis. The total symmetric representation is always denoted by A. Hence in

Table 2.1.3.4. Irreducible representations of the point group 3

3	E	D_{120}^z	D_{240}^z
$\boldsymbol{\tau}^{(1)}$	1	1	1
$\boldsymbol{\tau}^{(2)}$	1	$\exp(i2\pi/3)$	$\exp(-i2\pi/3)$
$\boldsymbol{\tau}^{(3)}$	1	$\exp(-i2\pi/3)$	$\exp(i2\pi/3)$

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Table 2.1.3.5. Irreducible representations of the space group $P6_3$ for $\mathbf{q} = \mathbf{0}$ (the Γ point)

$P6_3$	E	D_{60}^z	D_{120}^z	D_{180}^z	D_{240}^z	D_{300}^z
$\tau^{(1)}(\mathbf{0})$	1	1	1	1	1	1
$\tau^{(2)}(\mathbf{0})$	1	$\exp(i\pi/3)$	$\exp(i2\pi/3)$	-1	$\exp(i4\pi/3) = \exp(-i2\pi/3)$	$\exp(i5\pi/3) = \exp(-i\pi/3)$
$\tau^{(3)}(\mathbf{0})$	1	$\exp(i2\pi/3)$	$\exp(i4\pi/3) = \exp(-i2\pi/3)$	1	$\exp(i2\pi/3)$	$\exp(i4\pi/3) = \exp(-i2\pi/3)$
$\tau^{(4)}(\mathbf{0})$	1	-1	1	-1	1	-1
$\tau^{(5)}(\mathbf{0})$	1	$\exp(i4\pi/3) = \exp(-i2\pi/3)$	$\exp(i2\pi/3)$	1	$\exp(i4\pi/3) = \exp(-i2\pi/3)$	$\exp(i2\pi/3)$
$\tau^{(6)}(\mathbf{0})$	1	$\exp(i5\pi/3) = \exp(-i\pi/3)$	$\exp(i4\pi/3) = \exp(-i2\pi/3)$	-1	$\exp(i2\pi/3)$	$\exp(i\pi/3)$

Table 2.1.3.6. Irreducible representations of the space group $P6_3$ for $\mathbf{q} = \mathbf{c}^*/2$ (the A point)

$P6_3$	E	D_{60}^z	D_{120}^z	D_{180}^z	D_{240}^z	D_{300}^z
$\tau^{(1)}(\mathbf{c}^*/2)$	1	i	1	i	1	i
$\tau^{(2)}(\mathbf{c}^*/2)$	1	$i \exp(i\pi/3) = \exp(-i\pi/6)$	$\exp(i2\pi/3)$	- i	$\exp(i4\pi/3) = \exp(-i2\pi/3)$	$i \exp(-i\pi/3) = \exp(i\pi/6)$
$\tau^{(3)}(\mathbf{c}^*/2)$	1	$i \exp(i2\pi/3) = \exp(i\pi/6)$	$\exp(i4\pi/3) = \exp(-i2\pi/3)$	i	$\exp(i2\pi/3)$	$i \exp(-i2\pi/3) = \exp(-i\pi/6)$
$\tau^{(4)}(\mathbf{c}^*/2)$	1	- i	1	- i	1	- i
$\tau^{(5)}(\mathbf{c}^*/2)$	1	$i \exp(-i2\pi/3) = \exp(-i\pi/6)$	$\exp(i2\pi/3)$	i	$\exp(i4\pi/3) = \exp(-i2\pi/3)$	$i \exp(i2\pi/3) = \exp(i\pi/6)$
$\tau^{(6)}(\mathbf{c}^*/2)$	1	$i \exp(-i\pi/3) = \exp(i\pi/6)$	$\exp(i4\pi/3) = \exp(-i2\pi/3)$	- i	$\exp(i2\pi/3)$	$i \exp(i\pi/3) = \exp(-i\pi/6)$

the preceding example all the representations $\tau^{(2)}$, $\tau^{(3)}$, $\tau^{(5)}$ and $\tau^{(6)}$ are E-type representations since they are doubly degenerate at the zone centre due to time-reversal degeneracy. Moreover, $\tau^{(3)}$ and $\tau^{(5)}$ are symmetric with respect to D_{180}^z . Therefore, the irreducible representations of Fig. 2.1.3.9 can be identified as $A = \tau^{(1)}$, $B = \tau^{(2)}$, $E_1^- = \tau^{(2)}$, $E_1^+ = \tau^{(6)}$, $E_1^+ = \tau^{(5)}$ and $E_1^+ = \tau^{(3)}$.

It can be seen that all phonon branches cross the zone boundary continuously while changing their symmetry. This behaviour is a direct consequence of the time-reversal degeneracy.

2.1.3.6. Compatibility relations

In our last example, we recognized that the group of the wavevector consists of the same elements, irrespective of whether the Γ point, the zone-boundary A point or any other wavevector along the hexagonal axis is concerned. This behaviour, however, is the exception rather than the rule. In general, wavevectors on the Brillouin-zone boundary exhibit different point groups to wavevectors within the Brillouin zone and the Γ point yields the full point group of the crystal. Obviously, the symmetry of the lattice vibrations changes discontinuously when approaching prominent wavevectors. Phonon branches, on the other hand, represent continuous functions $\omega(\mathbf{q})$ within the reciprocal space. Hence the question arises as to how the different irreducible (multiplier) representations associated with one particular phonon branch at different wavevectors are interrelated, *i.e.* which of the individual representations are *compatible*.

The solution of this problem is quite simple as long as all of the irreducible multiplier representations are one-dimensional. For arbitrary wavevectors within the Brillouin zone, the point group $G_o(\mathbf{q})$ is always a subgroup of $G_o(0)$ as well as of $G_o(\mathbf{q}_{\text{BZ}})$, where

\mathbf{q}_{BZ} represents a wavevector at the Brillouin-zone boundary in the direction of \mathbf{q} . When leaving a prominent wavevector ($\mathbf{q} = \mathbf{0}$ or $\mathbf{q} = \mathbf{q}_{\text{BZ}}$), the transformation properties of lattice vibrations with respect to all those symmetry operations that are conserved do not change. Hence, the compatibility relations for one-dimensional irreducible multiplier representations can be formulated as

$$\tau(\mathbf{q}, \mathbf{R}) = \tau(\mathbf{0}, \mathbf{R}) = \tau(\mathbf{q}_{\text{BZ}}, \mathbf{R}) \quad \forall \mathbf{R} \in G_o(\mathbf{q}). \quad (2.1.3.67)$$

The simple relation (2.1.3.67) does not hold, however, if higher-dimensional representations have to be considered at prominent wavevectors. With respect only to the symmetry elements of the subgroup $G_o(\mathbf{q})$, those representations are not necessarily irreducible. Rather, they may be decomposed into several (up to three) irreducible components $\tau^{(s)}(\mathbf{q})$. The multiplicities are given by the characters using the following equation:

$$c_s = \sum_{\mathbf{R} \in G_o(\mathbf{q})} \chi_{\tau(\mathbf{0}, \mathbf{R})} \chi_{\tau^{(s)}(\mathbf{q}, \mathbf{R})} \quad (2.1.3.68)$$

or

$$c'_s = \sum_{\mathbf{R} \in G_o(\mathbf{q})} \chi_{\tau(\mathbf{q}_{\text{BZ}}, \mathbf{R})} \chi_{\tau^{(s)}(\mathbf{q}, \mathbf{R})}.$$

Hence, phonons corresponding to irreducible representations $\tau^{(s)}(\mathbf{q})$ with nonzero multiplicities c_s (c'_s) will mix at the Γ point (zone boundary) to yield degenerate modes corresponding to the higher-dimensional representation.

In conclusion, group theory provides an important tool not only for the labelling of lattice vibrations according to irreducible multiplier representations but also for the assignment of branches at points of degeneracy within the reciprocal space.

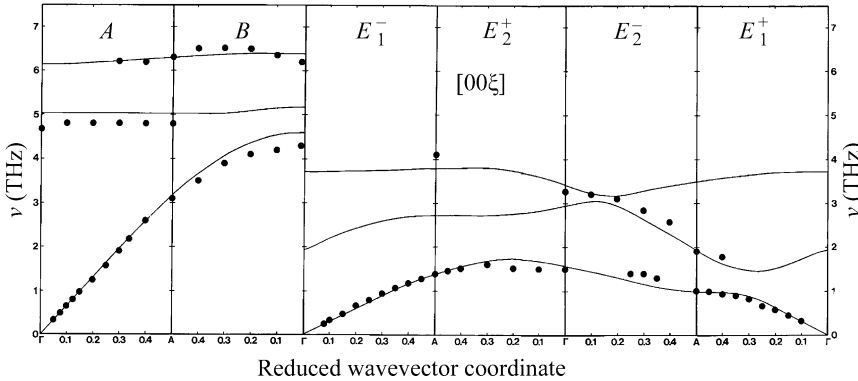


Fig. 2.1.3.9. Low-frequency part of the phonon dispersion of KLiSO_4 at room temperature (space group $P6_3$). The phonons are arranged in an extended zone scheme according to the different irreducible representations [after Eckold & Hahn (1987)]. The symbols represent experimental data and the lines represent the results of model calculations.

2.1.3.6.1. Example

To illustrate compatibility relations, let us once more consider the example of space group $P4mm$ as introduced in Sections 2.1.3.1.1, 2.1.3.3.1 and 2.1.3.4.1. For wavevectors along \mathbf{a}^* we have $G_o(\mathbf{q}) = \{E, m_y\}$ and there are two irreducible representations, a symmetric one (with respect to m_y) $\tau^+(\mathbf{q})$ with $\tau^+(\mathbf{q}, m_y) = 1$ and an antisymmetric one with $\tau^-(\mathbf{q}, m_y) = -1$. Remember the representations for the Γ point, shown in Table 2.1.3.7. We immediately recognize that the Γ -point representations $\tau^{(1^+)}(\mathbf{0})$ and $\tau^{(3^+)}(\mathbf{0})$ are related to the symmetric representation τ^+ for nonzero wavevectors along \mathbf{a}^* . $\tau^{(1^-)}(\mathbf{0})$ and $\tau^{(3^-)}(\mathbf{0})$, on the

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Table 2.1.3.7. Irreducible representations of the space group $P4mm$ for $\mathbf{q} = \mathbf{0}$ (the Γ point)

$P4mm$	Symmetry operation							
	E	D_{90}^z	D_{180}^z	D_{270}^z	m_x	m_y	$m_{[110]}$	$m_{[1\bar{1}0]}$
$\tau^{(1^+)}(\mathbf{0})$	$\mathbf{1}$	1	1	1	1	$\mathbf{1}$	1	1
$\tau^{(1^-)}(\mathbf{0})$	$\mathbf{1}$	1	1	1	-1	$-\mathbf{1}$	-1	-1
$\tau^{(3^+)}(\mathbf{0})$	$\mathbf{1}$	-1	1	-1	1	$\mathbf{1}$	-1	-1
$\tau^{(3^-)}(\mathbf{0})$	$\mathbf{1}$	-1	1	-1	-1	$-\mathbf{1}$	1	1
$\tau^{(2)}(\mathbf{0})$	$\begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & \mathbf{1} \end{pmatrix}$	$\begin{pmatrix} i & 0 \\ 0 & -i \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} -i & 0 \\ 0 & i \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} \mathbf{0} & -\mathbf{1} \\ -\mathbf{1} & \mathbf{0} \end{pmatrix}$	$\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & i \\ -i & 0 \end{pmatrix}$
$\chi_{\tau^{(2)}(\mathbf{0})}$	$\mathbf{2}$	0	-2	0	0	$\mathbf{0}$	0	0

other hand, are related to the antisymmetric representation τ^- .

The two-dimensional representation $\tau^{(2)}(\mathbf{0})$ exhibits the character $\chi_{\tau^{(2)}(\mathbf{0}, \mathbf{m}_y)} = 0$. When leaving the Γ point along \mathbf{a}^* , it therefore splits into the symmetric representation with $\chi_{\tau^+(\mathbf{q}, \mathbf{m}_y)} = 1$ and the antisymmetric one with $\chi_{\tau^-(\mathbf{q}, \mathbf{m}_y)} = -1$. Consequently, there are always pairs of a symmetric and an antisymmetric lattice vibration which degenerate at the Brillouin-zone centre and the phonon dispersion along \mathbf{a}^* exhibits the principal behaviour as shown in Fig. 2.1.3.10. Here, six modes are displayed which illustrate the six possibilities for relating symmetric and antisymmetric vibrations to the Γ -point representations.

2.1.3.7. Optical selection rules

Inelastic neutron scattering is the unique experimental method for the determination of phonons at arbitrary wavevectors. Additional information can be obtained by optical methods, infrared absorption and Raman spectroscopy. For the detection of lattice vibrations, electromagnetic radiation of appropriate frequencies in the THz regime is needed. The corresponding wavelengths are of the order of 10^{-2} cm and are therefore very large compared with typical lattice parameters. Consequently, optical spectroscopy is sensitive to long-wavelength phonons only, *i.e.* to Γ -point modes. Moreover, the visibility of lattice vibrations in infrared or Raman experiments is governed by selection rules which, in turn, are determined by the symmetry of the corresponding eigenvectors. We may distinguish infrared-active modes, Raman-active modes and 'silent' modes that are neither infrared- nor Raman-active. Some simple group-theoretical arguments lead to the criteria for infrared or Raman activity.

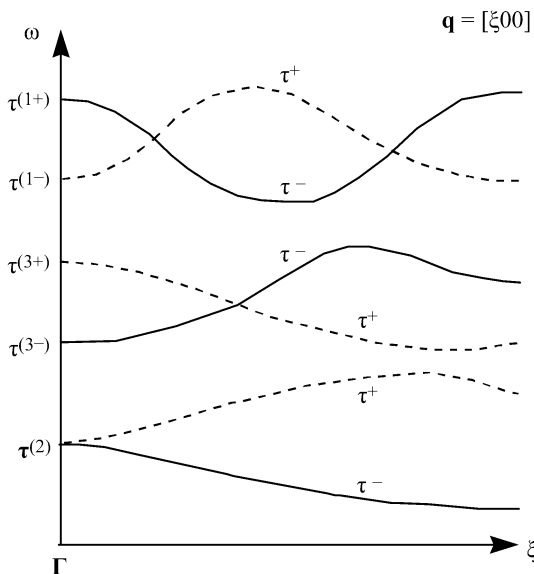


Fig. 2.1.3.10. Illustration of the compatibility relations for phonons in a tetragonal crystal with space group $P4mm$ for wavevectors along $[\xi 00]$.

Infrared spectroscopy is based on the absorption of electromagnetic radiation by phonons, as shown in Fig. 2.1.3.11. Photons can only be absorbed by those lattice vibrations that are associated with a periodic variation of an electric dipole moment. Since the dipole moment is a vector, it transforms under the symmetry operations of the crystal according to the vector representation τ_v , which is provided by the ordinary 3×3 matrices describing the effect of any rotation, mirror plane *etc.* upon an arbitrary vector of our three-dimensional space. It should be noted that the vector representation is in general reducible and can be regarded as the direct product of some irreducible representations. Lattice vibrations can carry an electric dipole moment only if their symmetry is compatible with the symmetry of a vector, *i.e.* if the corresponding irreducible representation is contained within the vector representation. The multiplicity of a particular irreducible Γ -point representation τ within the decomposition of the vector representation τ_v can be calculated from the respective characters χ_τ and χ_{τ_v} . Hence we may formulate the criterion for infrared activity as follows: Phonons corresponding to an irreducible representation τ are infrared active if

$$c_\tau = (1/|G|) \sum_{\mathbf{R}} \chi_\tau(\mathbf{R}) \chi_{\tau_v}(\mathbf{R}) \neq 0. \quad (2.1.3.69)$$

(First order) *Raman spectroscopy*, on the other hand, is based on the scattering of electromagnetic waves by phonons (see Fig. 2.1.3.12). Scattered intensity can only be obtained if the incident wave polarizes the crystal in such a way that it acts as a source for the outgoing wave. This is achieved if the tensor of the polarizability exhibits nonzero elements that relate electric field

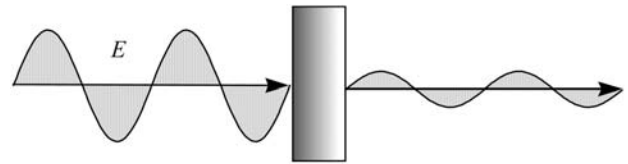


Fig. 2.1.3.11. Principle of infrared absorption.

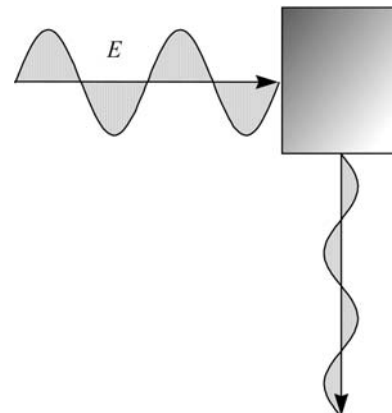


Fig. 2.1.3.12. Principle of Raman spectroscopy.

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Table 2.1.3.8. Character table of the space group $P4mm$ for $\mathbf{q} = \mathbf{0}$ (the Γ point)

$P4mm$	Symmetry operation							
	E	D_{90}^z	D_{180}^z	D_{270}^z	m_x	m_y	$m_{[110]}$	$m_{[1\bar{1}0]}$
$\chi_{\tau^{(1+)}}$	1	1	1	1	1	1	1	1
$\chi_{\tau^{(1-)}}$	1	1	1	1	-1	-1	-1	-1
$\chi_{\tau^{(3+)}}$	1	-1	1	-1	1	1	-1	-1
$\chi_{\tau^{(3-)}}$	1	-1	1	-1	-1	-1	1	1
$\chi_{\tau^{(2)}}$	2	0	-2	0	0	0	0	0
τ_v	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$
χ_{τ_v}	3	1	-1	1	1	1	1	1
χ_{τ_T}	6	0	2	0	2	2	2	2

components in the directions of the incident and scattered waves. Hence, only those lattice vibrations that are associated with a periodic variation of the polarizability tensor can yield (first-order) Raman intensity. Their symmetry has to be compatible with the symmetry of a tensor, *i.e.* the corresponding irreducible representation has to be contained within the (reducible) tensor representation τ_T . As for infrared activity, we may therefore formulate the criterion for Raman-active phonons with the help of the characters χ_{τ} and χ_{τ_v} : Phonons corresponding to an irreducible representation τ are Raman active if

$$c_{\tau} = (1/|G|) \sum_{\mathbf{R}} \chi_{\tau}(\mathbf{R}) \chi_{\tau_T}(\mathbf{R}) \neq 0. \quad (2.1.3.70)$$

Without going into details, we note that the tensor representation τ_T is the symmetric square of the vector representation τ_v and its character may be calculated from the character of τ_v ,

$$\chi_{\tau_T}(\mathbf{R}) = \frac{1}{2} [\chi_v^2(\mathbf{R}) + \chi_v(\mathbf{R}^2)]. \quad (2.1.3.71)$$

It should be noted that group-theoretical considerations yield *necessary conditions* for the visibility of phonons. They cannot predict, however, intensities of active modes since these depend on crystal-specific properties like dipole moments or elements of the polarizability tensor.

2.1.3.7.1. Example

As an example, let us once more consider the space group $P4mm$. For $\mathbf{q} = \mathbf{0}$, the character table shown in Table 2.1.3.8 summarizes all essential information about irreducible, vector and tensor representations. Obviously, the vector representation consists of the irreducible representations $\tau^{(1+)}$ and $\tau^{(2)}$, the latter being two-dimensional. Γ -point phonons corresponding to these two representations are infrared active. All other lattice vibrations cannot be detected by absorption experiments.

Using the multiplicities as calculated from (2.1.3.70), we obtain the decomposition of the tensor representation:

$$\tau_T = 2\tau^{(1+)} + \tau^{(3+)} + \tau^{(3-)} + \tau^{(2)}.$$

Hence phonons corresponding to the representations $\tau^{(1+)}$, $\tau^{(3+)}$, $\tau^{(3-)}$ and $\tau^{(2)}$ are Raman active.

All lattice vibrations that belong to the representation $\tau^{(1-)}$ are neither infrared nor Raman active. They cannot be detected in (first-order) optical experiments and are therefore called silent modes.

2.1.4. Conclusion

Phonon investigations provide one of the most powerful tools for the determination of interatomic interactions within crystals since the phonon dispersion reflects all aspects of microscopic forces acting between the individual atoms. The symmetry of the atomic arrangement leads to certain restrictions for the actual

type of lattice vibrations. In this chapter, we have presented the fundamental ideas about phonon dispersion with special emphasis on the symmetry properties of the vibrations of a lattice.

Experimental phonon data are frequently interpreted in terms of either phenomenological interatomic potentials or *ab initio* band-structure calculations. In most cases, rather specific models are used for the theoretical calculation of the phonon dispersion for particular substances. This aspect is, however, beyond the scope of the present article. The interested reader is therefore referred to the original literature and a compilation by Bilz & Kress (1979), where phonon dispersion curves for more than a hundred insulating crystals are collected.

In the present chapter we have restricted ourselves to the general aspects of the symmetry reduction of both the dynamical matrix and its eigenvectors. It has been shown that group-theoretical methods play an important role in the labelling of phonons, in the consideration of degeneracies and, in particular, in the correct interpretation of experimental results.

It should be added that there is a computer program written by Warren & Worlton (1974) that enables the calculation of symmetry coordinates for arbitrary structures, for example. As part of a general lattice-dynamical program package for phenomenological model calculations written by Eckold *et al.* (1987; see also Eckold, 1992), it provides the symmetry reduction of the dynamical matrix and the assignment of individual phonon modes to the respective irreducible multiplier representations.

2.1.5. Glossary

$\mathbf{a}^*, \mathbf{b}^*, \mathbf{c}^*$	reciprocal-lattice vectors
A	Helmholtz free energy
\mathbf{A}	element of the coset $\mathbf{S}_- \circ G_o(\mathbf{q})$
$\mathbf{C}(\mathbf{q}) = (C_{\kappa\kappa'}^{\alpha\beta}(\mathbf{q}))$	modified dynamical matrix
c_{ij}	elastic stiffness in Voigt notation
(c_{ijklm})	tensor of elastic stiffnesses
c_p	lattice heat capacity at constant pressure
$\tilde{c}_{\mathbf{q},j}$	contribution of phonon state (\mathbf{q}, j) to the heat capacity at constant volume
c_s	multiplicity of irreducible representation s
c_V	lattice heat capacity at constant volume
c_V^{Debye}	lattice heat capacity at constant volume according to the Debye model
c_V^{Einstein}	lattice heat capacity at constant volume according to the Einstein model
$\mathbf{D}(\mathbf{q}) = (D_{\kappa\kappa'}^{\alpha\beta}(\mathbf{q}))$	dynamical matrix
$\overline{\mathbf{D}}^{(s)}(\mathbf{q})$	submatrix of the block-diagonalized dynamical matrix corresponding to irreducible multiplier representation σ

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$\mathbf{D}_{\kappa\kappa'}$	3 × 3 submatrix of the dynamical matrix	\mathbf{S}_-	space-group element that inverts the wavevector
\mathbf{D}_α^i	matrix of rotation about axis i by the angle α	t	time
$\mathbf{e}_\kappa(\mathbf{q}, j)$	polarization vector of atom κ corresponding to the phonon (\mathbf{q}, j)	T	temperature
$\mathbf{e}(\mathbf{q}, j)$	eigenvector of the dynamical matrix corresponding to the phonon (\mathbf{q}, j)	$\mathbf{T}(\mathbf{q}, \mathbf{R})$ $= (T_{\kappa\kappa}^{\alpha\mu}(\mathbf{q}, \mathbf{R}))$	matrix operator associated with a symmetry operation \mathbf{r} of the point group of the wavevector \mathbf{q}
E	identity	\mathbf{u}^o	polarization vector for elastic waves
$\mathbf{E}(\mathbf{q}, s\alpha\lambda)$ $= (E_\kappa^\alpha(\mathbf{q}, s\alpha\lambda))$	matrix of symmetry coordinates	$\mathbf{u}_{\kappa l}(t)$	displacement vector of atom (κl)
E_o	zero-point energy	V	potential energy
E_{ph}	lattice energy	V	volume
$E_{\mathbf{q}, j}$	contribution of the phonon (\mathbf{q}, j) to the energy of the lattice	$\mathbf{V}(\kappa l, \kappa' l')$ $= (V_{\alpha\beta}(\kappa l, \kappa' l'))$	matrix of force constants acting between atoms (κl) and $(\kappa' l')$
$f_o(\kappa, S)$	atom transformation table	v_s	sound velocity
f_σ	degeneracy of the eigenfrequency $\omega_{\mathbf{q}, \sigma}$	$\mathbf{v}(\mathbf{S})$	fractional translation associated with symmetry operation \mathbf{S}
$\mathbf{F}(\mathbf{q}) = (\mathbf{F}_{\kappa, \kappa'}(\mathbf{q}))$	Fourier-transformed force-constant matrix	$\mathbf{x}(m)$	lattice translation
\mathbf{g}	reciprocal-lattice vector	Z	partition function
$G(\mathbf{q})$	space group of the wavevector \mathbf{q}	$\boldsymbol{\alpha} = (\alpha_{\kappa l})$	tensor of thermal expansion
$G_o(\mathbf{q})$	point group of the wavevector \mathbf{q}	β	coefficient of volume expansion
$G_o(\mathbf{q}, -\mathbf{q})$	augmented point group of the wavevector \mathbf{q}	γ	mean Grüneisen parameter
$ G $	order of group G	$\gamma_{\mathbf{q}, j}$	averaged-mode Grüneisen parameter
$G(\omega)$	density of phonon states	$\gamma_{\mathbf{q}, \kappa l}$	generalized-mode Grüneisen parameters
$G^{\text{Debye}}(\omega)$	density of phonon states according to the Debye model	$\boldsymbol{\Gamma} = (\Gamma_{jl})$	propagation tensor
$G^{\text{Einstein}}(\omega)$	density of phonon states according to the Einstein model	$\boldsymbol{\Gamma} = (\Gamma_{\kappa\kappa}^{\alpha\mu}(\mathbf{q}, \{\mathbf{S} \mathbf{v}(\mathbf{S}) + \mathbf{x}(m)\}))$	transformation matrix
H	Hamiltonian	$\delta_{\kappa l}$	Kronecker delta
\hbar	Planck constant (1.0546×10^{-34} J s)	$\delta(\omega)$	Dirac delta function
I	inversion	$\boldsymbol{\Delta}(\mathbf{q}, \mathbf{R})$	block-diagonal matrix of irreducible representations
k	Boltzmann constant (1.381×10^{-23} J K ⁻¹)	$\boldsymbol{\varepsilon} = (\varepsilon_{\kappa l})$	strain tensor
\mathbf{K}_o	anti-unitary operator	χ	character of a representation
\mathbf{M}	mass tensor	$\varphi(\mathbf{q}, \mathbf{r}_i, \mathbf{r}_j)$	multiplier associated with two symmetry operations \mathbf{r}_i and \mathbf{r}_j of the point group of the wavevector \mathbf{q}
m_i	mirror plane perpendicular to axis i	Φ	potential energy
m_κ	mass of atom κ	κ	isothermal compressibility
$n_{\mathbf{q}, j}$	Bose factor corresponding to the phonon state (\mathbf{q}, j)	Θ_D	Debye temperature
N	number of atoms within the primitive cell	Θ_E	Einstein temperature
N_Z	number of primitive cells	ρ	density
p	pressure	$\boldsymbol{\sigma} = (\sigma_{\kappa l})$	stress tensor
$\mathbf{p}_{\kappa l}$	momentum of atom (κl)	$\boldsymbol{\tau}^{(s)}(\mathbf{q}, \mathbf{R})$ $= (\tau_{\lambda\lambda}^{(s)}(\mathbf{q}, \mathbf{R}))$	irreducible representation
p_n	occupation probability of quantum state n	$\overline{\boldsymbol{\tau}^{(s)}}(\mathbf{q}, \mathbf{R})$	conjugated representation
$\mathbf{P}^{(s)}(\mathbf{q}) = (P_{\lambda\lambda}^{(s)}(\mathbf{q}))$	projection operator	$\boldsymbol{\tau}_v$	vector representation
\mathbf{q}	phonon wavevector	$\boldsymbol{\tau}_T$	tensor representation
\mathbf{q}_{BZ}	wavevector on the Brillouin-zone boundary	ω_D	Debye frequency
$Q_{\mathbf{q}, j}$	normal coordinate corresponding to the phonon (\mathbf{q}, j)	ω_E	Einstein frequency
\mathbf{r}_l	vector to the origin of the l th primitive cell	$\omega_{\mathbf{q}, j}$	frequency of phonon (\mathbf{q}, j)
$\mathbf{r}_{\kappa l}(t)$	time-dependent position vector of atom (κl)	$\boldsymbol{\Psi}$	arbitrary vector
\mathbf{r}_κ^o	equilibrium position of atom κ with respect to the origin of the primitive cell	*	denotes the complex-conjugate quantity
$\mathbf{r}_{\kappa l}^o$	equilibrium position of atom κ within the l th primitive cell	+	denotes the Hermitian conjugate matrix
\mathbf{R}	element of the point group of the wavevector $G_o(\mathbf{q})$	T	denotes the transposed matrix
$\bar{\mathbf{R}}$	element of $G_o(\mathbf{q}, -\mathbf{q})$		
$\{\mathbf{S} \mathbf{v}(\mathbf{S}) + \mathbf{x}(m)\}$	symmetry operation (Seitz notation)		
$\mathbf{S} = (S_{\alpha\beta})$	matrix of rotation		

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