$$\beta = \kappa \frac{c_V \gamma}{V}, \tag{2.1.2.84}$$

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,

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

and hence the following equation is obtained:

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

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

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

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

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

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:

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

[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]

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

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

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

or in submatrix notation

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

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*

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

or in matrix notation

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

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

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

[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.

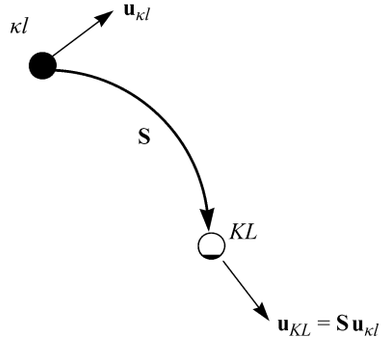

Fig. 2.1.3.1. Transformation of atomic displacements by a symmetry operation.

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

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

or

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

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

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

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

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

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 $D^{\mu\nu}_{\kappa\kappa'}(\mathbf{q})$. 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*

$$\begin{aligned} \mathbf{r}^o_{KL} = \mathbf{r}^o_K + \mathbf{r}_L &= \{\mathbf{S}|\mathbf{v}(\mathbf{S}) + \mathbf{x}(m)\}\, \mathbf{r}^o_{\kappa l} \\ &= \mathbf{S}\, \mathbf{r}^o_{\kappa l} + \mathbf{v}(\mathbf{S}) + \mathbf{x}(m) \\ &= \mathbf{S}\,(\mathbf{r}^o_\kappa + \mathbf{r}_l) + \mathbf{v}(\mathbf{S}) + \mathbf{x}(m) \end{aligned} \tag{2.1.3.9}$$

and

$$\begin{aligned} \mathbf{r}^o_\kappa + \mathbf{r}_l &= \mathbf{S}^{-1}\,(\mathbf{r}^o_K + \mathbf{r}_L) - \mathbf{v}(\mathbf{S}) - \mathbf{x}(m) \\ &= \{\mathbf{S}|\mathbf{v}(\mathbf{S}) + \mathbf{x}(m)\}^{-1}\, \mathbf{r}^o_K + \mathbf{S}^{-1}\, \mathbf{r}_L. \end{aligned} \tag{2.1.3.9a}$$

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

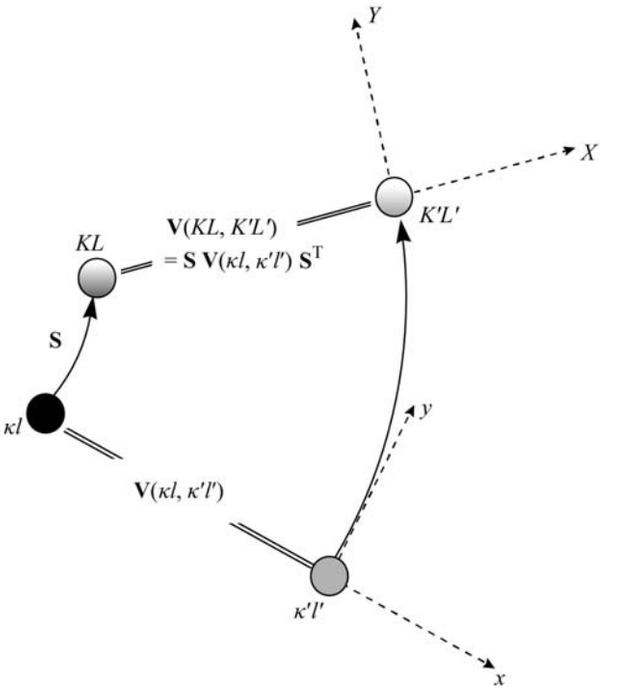

Fig. 2.1.3.2. Relation between interaction of symmetry-related atoms.

$$\mathbf{S}^{-1}\, \mathbf{r}_L = \mathbf{r}^o_\kappa + \mathbf{r}_l - \{\mathbf{S}|\mathbf{v}(\mathbf{S}) + \mathbf{x}(m)\}^{-1}\, \mathbf{r}^o_K. \tag{2.1.3.10}$$

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

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

or

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

or in submatrix notation

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

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

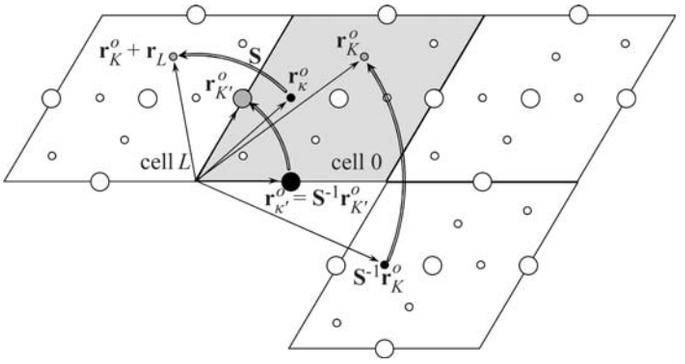

Fig. 2.1.3.3. Symmetry-related atoms in different primitive cells.

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

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

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

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

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

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

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:

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

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 $\mathbf{g}(\mathbf{q}, \mathbf{S})$,

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

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 $\{\mathbf{R}|\mathbf{v}(\mathbf{R}) + \mathbf{x}(m)\}$. The corresponding unitary and Hermitian transformation matrices can be reduced to

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

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

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

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

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

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:

$$T^{\alpha\mu}_{K\kappa}(\mathbf{q}, \mathbf{R}) = R_{\alpha\mu}\delta\big(\kappa, F_o^{-1}(K, \mathbf{R})\big) \exp[i\mathbf{q}\,(\mathbf{r}^o_K - \mathbf{R}\,\mathbf{r}^o_\kappa)]. \tag{2.1.3.19a}$$

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

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

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:

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

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

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

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.

[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 $\{\mathbf{S}|\mathbf{v}(\mathbf{S}) + \mathbf{x}(m)\}^{-1}\,\mathbf{r}^o_K - \mathbf{r}^o_\kappa$ 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 $\mathbf{q}' = \mathbf{q} + \mathbf{g}$.

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 **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)]:

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

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

$$\mathbf{S}_- \, \mathbf{q} = -\mathbf{q}. \tag{2.1.3.23}$$

Using equation (2.1.3.14) we obtain

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

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

$$\mathbf{K}_o \, \mathbf{\Psi} = \mathbf{\Psi}^*. \tag{2.1.3.25}$$

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

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

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

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

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

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

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 $\big((S_-)_{\alpha\beta} = -\delta_{\alpha\beta}\big)$, in particular, then (2.1.3.28) reduces to

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

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

$$C^{\alpha\beta}_{\kappa\kappa'}(\mathbf{q}) = \exp(-i\mathbf{q}\mathbf{r}_\kappa)\, D^{\alpha\beta}_{\kappa\kappa'}(\mathbf{q})\, \exp(i\mathbf{q}\mathbf{r}_{\kappa'}) \tag{2.1.3.30}$$

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 $\mathbf{\Gamma}(\mathbf{q}, \{\mathbf{S}|\mathbf{v}(\mathbf{S}) + \mathbf{x}(m)\})$ the anti-unitary operator $\mathbf{K}_o \, \mathbf{\Gamma}(\mathbf{q}, \{\mathbf{S}_-|\mathbf{v}(\mathbf{S}_-) + \mathbf{x}(m)\})$ 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

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

The **T** matrix operators provide a *multiplier corepresentation*. The multipliers are not uniquely defined as in equation (2.1.3.21*a*). 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:

$\bar{\mathbf{R}} \in G_o(\mathbf{q}, -\mathbf{q})$ 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

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

is determined by the multipliers

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

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 **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 *P*4*mm*, with lattice parameters *a* and *c*. The primitive cell spanned by the three mutually orthogonal vectors **a**, **b** and **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 *P*4*mm* contains eight symmetry operations, namely

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

[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.

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

(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 [110] axis, denoted $m_{[110]}$.
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 (2.1.3.19*a*), we can immediately write down the transformation matrix for any of these symmetry operations. Using the notation

$$\mathbf{E} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \mathbf{D}^z_{90} = \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\mathbf{D}^z_{180} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \mathbf{D}^z_{270} = \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\mathbf{m}_x = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \mathbf{m}_y = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\mathbf{m}_{[\bar{1}10]} = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \mathbf{m}_{[110]} = \begin{pmatrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

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

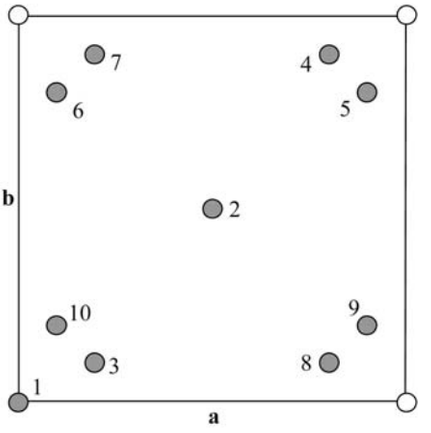

Fig. 2.1.3.4. Projection along the tetragonal z axis of the example structure given in Table 2.1.3.1.

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

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

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

Table 2.1.3.2. *Atom transformation table*

P4mm	Symmetry operation							
Atom No.	E	D^z_{90}	D^z_{180}	D^z_{270}	m_x	m_y	$m_{[\bar{1}10]}$	$m_{[110]}$
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	$4-\mathbf{a}-\mathbf{b}$

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

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

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

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

and

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

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 $\mathbf{D}_{\kappa\kappa'}(\mathbf{0})$ submatrices:

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

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

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

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

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

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

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

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

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

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^z_{180} and m_x. Hence the enlarged group $G_o(\mathbf{q}, -\mathbf{q})$ consists of the elements E, m_y, m_x and D^z_{180}. Inspection of the atom transformation table yields the remaining matrix operators:

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

and

$$\mathbf{T}(h\mathbf{a}^*, \mathbf{m}_x) = \exp(-2\pi i h) \begin{pmatrix} \mathbf{m}_x \exp(2\pi i h) & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \mathbf{m}_x & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & \mathbf{m}_x & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \mathbf{m}_x & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \mathbf{m}_x & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \mathbf{m}_x & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \mathbf{m}_x & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \mathbf{m}_x & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \mathbf{m}_x \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \mathbf{m}_x & 0 \end{pmatrix} \mathbf{K}_o .$$

Being anti-unitary, the corresponding inverse operators are[7]

$$\mathbf{T}^{-1}(h\mathbf{a}^*, \mathbf{D}^z_{180}) = \mathbf{K}_o\, \mathbf{T}^{+}(h\mathbf{a}^*, \mathbf{D}^z_{180}),$$
$$\mathbf{T}^{-1}(h\mathbf{a}^*, \mathbf{m}_x) = \mathbf{K}_o\, \mathbf{T}^{+}(h\mathbf{a}^*, \mathbf{m}_x).$$

The invariance of the dynamical matrix with respect to the similarity transformation ($\mathbf{T}^{-1}\,\mathbf{D}\,\mathbf{T} = \mathbf{D}$) using any of these operators leads to the following relations for wavevectors along $\mathbf{a}^*$:[8]

For $\mathbf{R} = \mathbf{m}_y$:

$$\begin{pmatrix} \mathbf{D}_{11} & \mathbf{D}_{12} & \mathbf{D}_{13} & \mathbf{D}_{14} & \mathbf{D}_{15} & \mathbf{D}_{16} & \mathbf{D}_{17} & \mathbf{D}_{18} & \mathbf{D}_{19} & \mathbf{D}_{1,10} \\ & \mathbf{D}_{22} & \mathbf{D}_{23} & \mathbf{D}_{24} & \mathbf{D}_{25} & \mathbf{D}_{26} & \mathbf{D}_{27} & \mathbf{D}_{28} & \mathbf{D}_{29} & \mathbf{D}_{2,10} \\ & & \mathbf{D}_{33} & \mathbf{D}_{34} & \mathbf{D}_{35} & \mathbf{D}_{36} & \mathbf{D}_{37} & \mathbf{D}_{38} & \mathbf{D}_{39} & \mathbf{D}_{3,10} \\ & & & \mathbf{D}_{44} & \mathbf{D}_{45} & \mathbf{D}_{46} & \mathbf{D}_{47} & \mathbf{D}_{48} & \mathbf{D}_{49} & \mathbf{D}_{4,10} \\ & & & & \mathbf{D}_{55} & \mathbf{D}_{56} & \mathbf{D}_{57} & \mathbf{D}_{58} & \mathbf{D}_{59} & \mathbf{D}_{5,10} \\ & & & & & \mathbf{D}_{66} & \mathbf{D}_{67} & \mathbf{D}_{68} & \mathbf{D}_{69} & \mathbf{D}_{6,10} \\ & & & & & & \mathbf{D}_{77} & \mathbf{D}_{78} & \mathbf{D}_{79} & \mathbf{D}_{7,10} \\ & & & & & & & \mathbf{D}_{88} & \mathbf{D}_{89} & \mathbf{D}_{8,10} \\ & & & & & & & & \mathbf{D}_{99} & \mathbf{D}_{9,10} \\ & & & & & & & & & \mathbf{D}_{10,10} \end{pmatrix}$$

$$= \begin{pmatrix} \tilde{\mathbf{D}}_{11} & \tilde{\mathbf{D}}_{12} & \tilde{\mathbf{D}}_{17} & \tilde{\mathbf{D}}_{18} & \tilde{\mathbf{D}}_{19} & \tilde{\mathbf{D}}_{1,10} & \tilde{\mathbf{D}}_{13} & \tilde{\mathbf{D}}_{14} & \tilde{\mathbf{D}}_{15} & \tilde{\mathbf{D}}_{16} \\ & \tilde{\mathbf{D}}_{22} & \tilde{\mathbf{D}}_{27} & \tilde{\mathbf{D}}_{28} & \tilde{\mathbf{D}}_{29} & \tilde{\mathbf{D}}_{2,10} & \tilde{\mathbf{D}}_{23} & \tilde{\mathbf{D}}_{24} & \tilde{\mathbf{D}}_{25} & \tilde{\mathbf{D}}_{26} \\ & & \tilde{\mathbf{D}}_{77} & \tilde{\mathbf{D}}_{78} & \tilde{\mathbf{D}}_{79} & \tilde{\mathbf{D}}_{7,10} & \tilde{\mathbf{D}}_{73} & \tilde{\mathbf{D}}_{74} & \tilde{\mathbf{D}}_{75} & \tilde{\mathbf{D}}_{76} \\ & & & \tilde{\mathbf{D}}_{88} & \tilde{\mathbf{D}}_{89} & \tilde{\mathbf{D}}_{8,10} & \tilde{\mathbf{D}}_{83} & \tilde{\mathbf{D}}_{84} & \tilde{\mathbf{D}}_{85} & \tilde{\mathbf{D}}_{86} \\ & & & & \tilde{\mathbf{D}}_{99} & \tilde{\mathbf{D}}_{9,10} & \tilde{\mathbf{D}}_{93} & \tilde{\mathbf{D}}_{94} & \tilde{\mathbf{D}}_{95} & \tilde{\mathbf{D}}_{96} \\ & & & & & \tilde{\mathbf{D}}_{10,10} & \tilde{\mathbf{D}}_{10,3} & \tilde{\mathbf{D}}_{10,4} & \tilde{\mathbf{D}}_{10,5} & \tilde{\mathbf{D}}_{10,6} \\ & & & & & & \tilde{\mathbf{D}}_{33} & \tilde{\mathbf{D}}_{34} & \tilde{\mathbf{D}}_{35} & \tilde{\mathbf{D}}_{36} \\ & & & & & & & \tilde{\mathbf{D}}_{44} & \tilde{\mathbf{D}}_{45} & \tilde{\mathbf{D}}_{46} \\ & & & & & & & & \tilde{\mathbf{D}}_{55} & \tilde{\mathbf{D}}_{56} \\ & & & & & & & & & \tilde{\mathbf{D}}_{66} \end{pmatrix},$$

with $\tilde{\mathbf{D}}_{kl} = \mathbf{m}_y\, \mathbf{D}_{kl}\, \mathbf{m}_y = \begin{pmatrix} D^{11}_{kl} & -D^{12}_{kl} & D^{13}_{kl} \\ -D^{21}_{kl} & D^{22}_{kl} & -D^{23}_{kl} \\ D^{31}_{kl} & -D^{32}_{kl} & D^{33}_{kl} \end{pmatrix}$

for $\mathbf{R} = \mathbf{D}^z_{180}$:

$$\begin{pmatrix} \mathbf{D}_{11} & \mathbf{D}_{12} & \mathbf{D}_{13} & \mathbf{D}_{14} & \mathbf{D}_{15} & \mathbf{D}_{16} & \mathbf{D}_{17} & \mathbf{D}_{18} & \mathbf{D}_{19} & \mathbf{D}_{1,10} \\ & \mathbf{D}_{22} & \mathbf{D}_{23} & \mathbf{D}_{24} & \mathbf{D}_{25} & \mathbf{D}_{26} & \mathbf{D}_{27} & \mathbf{D}_{28} & \mathbf{D}_{29} & \mathbf{D}_{2,10} \\ & & \mathbf{D}_{33} & \mathbf{D}_{34} & \mathbf{D}_{35} & \mathbf{D}_{36} & \mathbf{D}_{37} & \mathbf{D}_{38} & \mathbf{D}_{39} & \mathbf{D}_{3,10} \\ & & & \mathbf{D}_{44} & \mathbf{D}_{45} & \mathbf{D}_{46} & \mathbf{D}_{47} & \mathbf{D}_{48} & \mathbf{D}_{49} & \mathbf{D}_{4,10} \\ & & & & \mathbf{D}_{55} & \mathbf{D}_{56} & \mathbf{D}_{57} & \mathbf{D}_{58} & \mathbf{D}_{59} & \mathbf{D}_{5,10} \\ & & & & & \mathbf{D}_{66} & \mathbf{D}_{67} & \mathbf{D}_{68} & \mathbf{D}_{69} & \mathbf{D}_{6,10} \\ & & & & & & \mathbf{D}_{77} & \mathbf{D}_{78} & \mathbf{D}_{79} & \mathbf{D}_{7,10} \\ & & & & & & & \mathbf{D}_{88} & \mathbf{D}_{89} & \mathbf{D}_{8,10} \\ & & & & & & & & \mathbf{D}_{99} & \mathbf{D}_{9,10} \\ & & & & & & & & & \mathbf{D}_{10,10} \end{pmatrix}$$

$$= \begin{pmatrix} \tilde{\mathbf{D}}^*_{11} & \tilde{\mathbf{D}}^*_{12} & \tilde{\mathbf{D}}^*_{14} & \tilde{\mathbf{D}}^*_{13} & \tilde{\mathbf{D}}^*_{1,10} & \tilde{\mathbf{D}}^*_{19} & \tilde{\mathbf{D}}^*_{18} & \tilde{\mathbf{D}}^*_{17} & \tilde{\mathbf{D}}^*_{16} & \tilde{\mathbf{D}}^*_{15} \\ & \tilde{\mathbf{D}}^*_{22} & \tilde{\mathbf{D}}^*_{24} & \tilde{\mathbf{D}}^*_{23} & \tilde{\mathbf{D}}^*_{2,10} & \tilde{\mathbf{D}}^*_{29} & \tilde{\mathbf{D}}^*_{28} & \tilde{\mathbf{D}}^*_{27} & \tilde{\mathbf{D}}^*_{26} & \tilde{\mathbf{D}}^*_{25} \\ & & \tilde{\mathbf{D}}^*_{44} & \tilde{\mathbf{D}}^*_{43} & \tilde{\mathbf{D}}^*_{4,10} & \tilde{\mathbf{D}}^*_{49} & \tilde{\mathbf{D}}^*_{48} & \tilde{\mathbf{D}}^*_{47} & \tilde{\mathbf{D}}^*_{46} & \tilde{\mathbf{D}}^*_{45} \\ & & & \tilde{\mathbf{D}}^*_{33} & \tilde{\mathbf{D}}^*_{3,10} & \tilde{\mathbf{D}}^*_{39} & \tilde{\mathbf{D}}^*_{38} & \tilde{\mathbf{D}}^*_{37} & \tilde{\mathbf{D}}^*_{36} & \tilde{\mathbf{D}}^*_{35} \\ & & & & \tilde{\mathbf{D}}^*_{10,10} & \tilde{\mathbf{D}}^*_{10,9} & \tilde{\mathbf{D}}^*_{10,8} & \tilde{\mathbf{D}}^*_{10,7} & \tilde{\mathbf{D}}^*_{10,6} & \tilde{\mathbf{D}}^*_{10,5} \\ & & & & & \tilde{\mathbf{D}}^*_{99} & \tilde{\mathbf{D}}^*_{98} & \tilde{\mathbf{D}}^*_{97} & \tilde{\mathbf{D}}^*_{96} & \tilde{\mathbf{D}}^*_{95} \\ & & & & & & \tilde{\mathbf{D}}^*_{88} & \tilde{\mathbf{D}}^*_{87} & \tilde{\mathbf{D}}^*_{86} & \tilde{\mathbf{D}}^*_{85} \\ & & & & & & & \tilde{\mathbf{D}}^*_{77} & \tilde{\mathbf{D}}^*_{76} & \tilde{\mathbf{D}}^*_{75} \\ & & & & & & & & \tilde{\mathbf{D}}^*_{66} & \tilde{\mathbf{D}}^*_{65} \\ & & & & & & & & & \tilde{\mathbf{D}}^*_{55} \end{pmatrix}$$

with $\tilde{\mathbf{D}}_{kl} = \mathbf{D}^z_{180}\, \mathbf{D}_{kl}\, \mathbf{D}^z_{180} = \begin{pmatrix} D^{11}_{kl} & D^{12}_{kl} & -D^{13}_{kl} \\ D^{21}_{kl} & D^{22}_{kl} & -D^{23}_{kl} \\ -D^{31}_{kl} & -D^{32}_{kl} & D^{33}_{kl} \end{pmatrix}$

and

for $\mathbf{R} = \mathbf{m}_x$:

$$\begin{pmatrix} \mathbf{D}_{11} & \mathbf{D}_{12} & \mathbf{D}_{13} & \mathbf{D}_{14} & \mathbf{D}_{15} & \mathbf{D}_{16} & \mathbf{D}_{17} & \mathbf{D}_{18} & \mathbf{D}_{19} & \mathbf{D}_{1,10} \\ & \mathbf{D}_{22} & \mathbf{D}_{23} & \mathbf{D}_{24} & \mathbf{D}_{25} & \mathbf{D}_{26} & \mathbf{D}_{27} & \mathbf{D}_{28} & \mathbf{D}_{29} & \mathbf{D}_{2,10} \\ & & \mathbf{D}_{33} & \mathbf{D}_{34} & \mathbf{D}_{35} & \mathbf{D}_{36} & \mathbf{D}_{37} & \mathbf{D}_{38} & \mathbf{D}_{39} & \mathbf{D}_{3,10} \\ & & & \mathbf{D}_{44} & \mathbf{D}_{45} & \mathbf{D}_{46} & \mathbf{D}_{47} & \mathbf{D}_{48} & \mathbf{D}_{49} & \mathbf{D}_{4,10} \\ & & & & \mathbf{D}_{55} & \mathbf{D}_{56} & \mathbf{D}_{57} & \mathbf{D}_{58} & \mathbf{D}_{59} & \mathbf{D}_{5,10} \\ & & & & & \mathbf{D}_{66} & \mathbf{D}_{67} & \mathbf{D}_{68} & \mathbf{D}_{69} & \mathbf{D}_{6,10} \\ & & & & & & \mathbf{D}_{77} & \mathbf{D}_{78} & \mathbf{D}_{79} & \mathbf{D}_{7,10} \\ & & & & & & & \mathbf{D}_{88} & \mathbf{D}_{89} & \mathbf{D}_{8,10} \\ & & & & & & & & \mathbf{D}_{99} & \mathbf{D}_{9,10} \\ & & & & & & & & & \mathbf{D}_{10,10} \end{pmatrix}$$

$$= \begin{pmatrix} \tilde{\mathbf{D}}^*_{11} & \tilde{\mathbf{D}}^*_{12} & \tilde{\mathbf{D}}^*_{18} & \tilde{\mathbf{D}}^*_{17} & \tilde{\mathbf{D}}^*_{16} & \tilde{\mathbf{D}}^*_{15} & \tilde{\mathbf{D}}^*_{14} & \tilde{\mathbf{D}}^*_{13} & \tilde{\mathbf{D}}^*_{1,10} & \tilde{\mathbf{D}}^*_{19} \\ & \tilde{\mathbf{D}}^*_{22} & \tilde{\mathbf{D}}^*_{28} & \tilde{\mathbf{D}}^*_{27} & \tilde{\mathbf{D}}^*_{26} & \tilde{\mathbf{D}}^*_{25} & \tilde{\mathbf{D}}^*_{24} & \tilde{\mathbf{D}}^*_{23} & \tilde{\mathbf{D}}^*_{2,10} & \tilde{\mathbf{D}}^*_{29} \\ & & \tilde{\mathbf{D}}^*_{88} & \tilde{\mathbf{D}}^*_{87} & \tilde{\mathbf{D}}^*_{86} & \tilde{\mathbf{D}}^*_{85} & \tilde{\mathbf{D}}^*_{84} & \tilde{\mathbf{D}}^*_{83} & \tilde{\mathbf{D}}^*_{8,10} & \tilde{\mathbf{D}}^*_{89} \\ & & & \tilde{\mathbf{D}}^*_{77} & \tilde{\mathbf{D}}^*_{76} & \tilde{\mathbf{D}}^*_{75} & \tilde{\mathbf{D}}^*_{74} & \tilde{\mathbf{D}}^*_{73} & \tilde{\mathbf{D}}^*_{7,10} & \tilde{\mathbf{D}}^*_{79} \\ & & & & \tilde{\mathbf{D}}^*_{66} & \tilde{\mathbf{D}}^*_{65} & \tilde{\mathbf{D}}^*_{64} & \tilde{\mathbf{D}}^*_{63} & \tilde{\mathbf{D}}^*_{6,10} & \tilde{\mathbf{D}}^*_{69} \\ & & & & & \tilde{\mathbf{D}}^*_{55} & \tilde{\mathbf{D}}^*_{54} & \tilde{\mathbf{D}}^*_{53} & \tilde{\mathbf{D}}^*_{5,10} & \tilde{\mathbf{D}}^*_{59} \\ & & & & & & \tilde{\mathbf{D}}^*_{44} & \tilde{\mathbf{D}}^*_{43} & \tilde{\mathbf{D}}^*_{4,10} & \tilde{\mathbf{D}}^*_{49} \\ & & & & & & & \tilde{\mathbf{D}}^*_{33} & \tilde{\mathbf{D}}^*_{3,10} & \tilde{\mathbf{D}}^*_{39} \\ & & & & & & & & \tilde{\mathbf{D}}^*_{10,10} & \tilde{\mathbf{D}}^*_{10,9} \\ & & & & & & & & & \tilde{\mathbf{D}}^*_{99} \end{pmatrix}$$

with $\tilde{\mathbf{D}}_{kl} = \mathbf{m}_x\, \mathbf{D}_{kl}\, \mathbf{m}_x = \begin{pmatrix} D^{11}_{kl} & -D^{12}_{kl} & -D^{13}_{kl} \\ -D^{21}_{kl} & D^{22}_{kl} & D^{23}_{kl} \\ -D^{31}_{kl} & D^{32}_{kl} & D^{33}_{kl} \end{pmatrix}$.

For the submatrix $\mathbf{D}_{11}$ (and similarly also for $\mathbf{D}_{12}$ and $\mathbf{D}_{22}$) we can combine the three relations and obtain

$$\mathbf{D}_{11} = \mathbf{m}_x\, \mathbf{D}^*_{11}\, \mathbf{m}_x = \begin{pmatrix} D^{11*}_{11} & -D^{12*}_{11} & -D^{13*}_{11} \\ -D^{12}_{11} & D^{22*}_{11} & D^{23*}_{11} \\ -D^{13}_{11} & D^{23}_{11} & D^{33*}_{11} \end{pmatrix}$$
$$= \mathbf{m}_y\, \mathbf{D}_{11}\, \mathbf{m}_y = \begin{pmatrix} D^{11}_{11} & -D^{12}_{11} & D^{13}_{11} \\ -D^{12*}_{11} & D^{22}_{11} & -D^{23}_{11} \\ D^{13*}_{11} & -D^{23*}_{11} & D^{33}_{11} \end{pmatrix}$$
$$= \mathbf{D}^z_{180}\, \mathbf{D}^*_{11}\, \mathbf{D}^z_{180} = \begin{pmatrix} D^{11*}_{11} & D^{12*}_{11} & -D^{13*}_{11} \\ D^{12}_{11} & D^{22*}_{11} & -D^{23*}_{11} \\ -D^{13}_{11} & -D^{23}_{11} & D^{33*}_{11} \end{pmatrix}.$$

[7] $\mathbf{T}^{+}$ denotes the Hermitian conjugate matrix.
[8] Note that the lower half of the Hermitian matrix in each case is omitted for clarity.

Hence

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

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:

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

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

$$\mathbf{D}(\mathbf{S}\,\mathbf{q})\,\mathbf{e}(\mathbf{S}\,\mathbf{q}, j) = \omega^2_{(\mathbf{S}\,\mathbf{q}),j}\,\mathbf{e}(\mathbf{S}\,\mathbf{q}, j) \tag{2.1.3.35}$$

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

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

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

$$\omega^2_{(\mathbf{S}\,\mathbf{q}),j} = \omega^2_{\mathbf{q},j}. \tag{2.1.3.37}$$

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

$$\omega^2_{(\mathbf{S}\,\mathbf{q}),j} = \omega^2_{\mathbf{q},j'}. \tag{2.1.3.37a}$$

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

$$\mathbf{D}(-\mathbf{q})\,\mathbf{e}(-\mathbf{q}, j) = \mathbf{D}^{*}(\mathbf{q})\,\mathbf{e}(-\mathbf{q}, j) = \omega^2_{-\mathbf{q},j}\,\mathbf{e}(-\mathbf{q}, j). \tag{2.1.3.38}$$

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

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

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

$$\omega_{-\mathbf{q},j} = \omega_{\mathbf{q},j}. \tag{2.1.3.39}$$

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

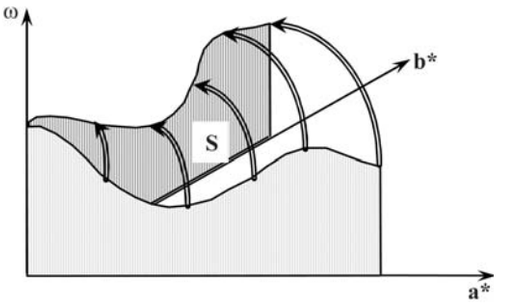

Fig. 2.1.3.5. Symmetry of the dispersion surface.

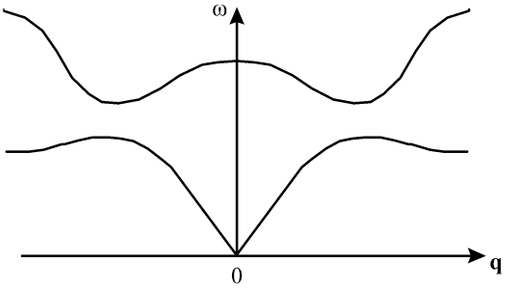

Fig. 2.1.3.6. The dispersion relation is an even function of $\mathbf{q}$.

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 $\mathbf{\Gamma}^{+}(\mathbf{q}, \{\mathbf{S}|\mathbf{v}(\mathbf{S}) + \mathbf{x}(m)\}\,\mathbf{e}(\mathbf{S}\,\mathbf{q}, j)$. If the corresponding eigenvalue $\omega^2_{\mathbf{q},j}$ is not degenerate, the (normalized) eigenvectors are uniquely determined except for a phase factor of unit modulus. Hence, the following relation holds:

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

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 $(\mathbf{S}\,\mathbf{q})\,\mathbf{x}(m)$, we obtain the simple form of the transformation law

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

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,

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 (2.1.3.19*a*). 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 $\omega^2_{\mathbf{q},j}$ as well as $\mathbf{e}(\mathbf{q}, j)$:

$$\mathbf{D}(\mathbf{q})\,\{\mathbf{T}(\mathbf{q}, \mathbf{R})\,\mathbf{e}(\mathbf{q}, j)\} = \omega^2_{\mathbf{q},j}\,\{\mathbf{T}(\mathbf{q}, \mathbf{R})\,\mathbf{e}(\mathbf{q}, j)\}. \qquad (2.1.3.42)$$

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

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

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

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

Obviously, the eigenvectors $\mathbf{e}(\mathbf{q}, \sigma\lambda)$ ($\lambda = 1, \ldots, f_\sigma$) 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 $\tau^{(\sigma)}_{\lambda\lambda'}(\mathbf{q}, \mathbf{R})$ 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:

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

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

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

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 $\boldsymbol{\Delta}(\mathbf{q}, \mathbf{R})$ has block-diagonal form. Moreover, each block on the diagonal consists of the matrix of a particular irreducible multiplier representation:

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

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 $\boldsymbol{\Delta}(\mathbf{q}, \mathbf{R})$ 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 $1, \ldots, c_s$. Using this notation, the transformation law for the eigenvectors can be rewritten as

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

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.

$$\chi(\mathbf{q},\mathbf{R}) = \sum_{\kappa\alpha} T^{\alpha\alpha}_{\kappa\kappa}(\mathbf{q},\mathbf{R}) = \sum_{\kappa\alpha} R_{\alpha\alpha}\,\delta(\kappa, F_o(\kappa,\mathbf{R}))\,\exp[i\mathbf{q}(\mathbf{r}_\kappa - \mathbf{R}\mathbf{r}_\kappa)] \tag{2.1.3.48}$$

and

$$\chi^{(s)}(\mathbf{q},\mathbf{R}) = \sum_{\lambda=1}^{f_s} \tau^{(s)}_{\lambda\lambda}(\mathbf{q},\mathbf{R}) \tag{2.1.3.49}$$

according to

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

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 4*mm*. It contains all eight symmetry operations and there are five different irreducible representations, denoted $\tau^{(1^+)}$, $\tau^{(1^-)}$, $\tau^{(3^+)}$, $\tau^{(3^-)}$ and $\boldsymbol{\tau}^{(2)}$. The corresponding character table including the reducible representation provided by the **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 $\boldsymbol{\tau}^{(2)}$ 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 **T** representation. As the result we obtain

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

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 $\boldsymbol{\tau}^{(2)}$, 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 **T**-matrix operators and the representation matrices $\boldsymbol{\tau}^{(s)}(\mathbf{q},\mathbf{R})$ of a particular irreducible multiplier representation we may define another matrix operator $\mathbf{P}^{(s)}(\mathbf{q})$ with the elements

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

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

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

we obtain

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

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

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

which can also be written in the form

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

	Symmetry operation							
4*mm*	E	D^z_{90}	D^z_{180}	D^z_{270}	m_x	m_y	$m_{[\bar{1}10]}$	$m_{[110]}$
χ_T	30	2	−2	2	2	2	2	2
$\chi_{\tau^{(1^+)}}$	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
$\boldsymbol{\tau}^{(2)}$	$\begin{pmatrix}1&0\\0&1\end{pmatrix}$	$\begin{pmatrix}i&0\\0&-i\end{pmatrix}$	$\begin{pmatrix}-1&0\\0&-1\end{pmatrix}$	$\begin{pmatrix}-i&0\\0&i\end{pmatrix}$	$\begin{pmatrix}0&1\\1&0\end{pmatrix}$	$\begin{pmatrix}0&-1\\-1&0\end{pmatrix}$	$\begin{pmatrix}0&-i\\i&0\end{pmatrix}$	$\begin{pmatrix}1&i\\-i&0\end{pmatrix}$
$\chi_{\boldsymbol{\tau}^{(2)}}$	2	0	−2	0	0	0	0	0

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

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

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

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 $\mathbf{E}(\mathbf{q}, s\lambda)$, $\lambda = 1, \ldots, f_s$, 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 $\mathbf{e}(\mathbf{q}, sa\lambda)$, $a = 1, \ldots, c_s$. By an appropriate choice of the different generating vectors $\mathbf{\Psi}_a$ 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 $\bar{D}^{s'a'\lambda'}_{sa\lambda}(\mathbf{q})$ $(\lambda = 1, \ldots, f_s,$ $a = 1, \ldots, c_s)$ and the components of the symmetry coordinates by $E^{\alpha}_{\kappa}(\mathbf{q}, sa\lambda)$ $(\kappa = 1, \ldots, N,\ \alpha = 1, 2, 3)$. 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):

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

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

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

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):

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

The elements of the submatrices are given by

$$\overline{D}^{(s)}_{aa'}(\mathbf{q}) = \sum_{\kappa\alpha}\sum_{\kappa'\beta} E^{\alpha*}_{\kappa}(\mathbf{q}, sa\lambda)\, D^{\alpha\beta}_{\kappa\kappa'}(\mathbf{q})\, E^{\beta}_{\kappa'}(\mathbf{q}, sa'\lambda), \tag{2.1.3.58}$$

and must be independent of λ. Obviously, a submatrix $\overline{\mathbf{D}}^{(s)}(\mathbf{q})$ 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 $\overline{\mathbf{D}}^{(s)}(\mathbf{q})$ 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):

$$\mathbf{P}^{(1^{\pm})}_{11}(\mathbf{0}) = \frac{1}{8}\begin{pmatrix}
\mathbf{\Sigma}_1^{\pm} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & \mathbf{\Sigma}_1^{\pm} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & \mathbf{E} & \mathbf{D}^{z}_{\bar{1}80} & \pm\mathbf{m}_{[110]} & \mathbf{D}^{z}_{90} & \pm\mathbf{m}_{y} & \pm\mathbf{m}_{x} & \mathbf{D}^{z}_{\bar{2}70} & \pm\mathbf{m}_{[\bar{1}10]} \\
0 & 0 & \mathbf{D}^{z}_{\bar{1}80} & \mathbf{E} & \pm\mathbf{m}_{[\bar{1}10]} & \mathbf{D}^{z}_{\bar{2}70} & \pm\mathbf{m}_{x} & \pm\mathbf{m}_{y} & \mathbf{D}^{z}_{90} & \pm\mathbf{m}_{[110]} \\
0 & 0 & \pm\mathbf{m}_{[110]} & \pm\mathbf{m}_{[\bar{1}10]} & \mathbf{E} & \pm\mathbf{m}_{x} & \mathbf{D}^{z}_{\bar{2}70} & \mathbf{D}^{z}_{90} & \pm\mathbf{m}_{y} & \mathbf{D}^{z}_{\bar{1}80} \\
0 & 0 & \mathbf{D}^{z}_{\bar{2}70} & \mathbf{D}^{z}_{90} & \pm\mathbf{m}_{x} & \mathbf{E} & \pm\mathbf{m}_{[110]} & \pm\mathbf{m}_{[\bar{1}10]} & \mathbf{D}^{z}_{\bar{1}80} & \pm\mathbf{m}_{y} \\
0 & 0 & \pm\mathbf{m}_{y} & \pm\mathbf{m}_{x} & \mathbf{D}^{z}_{90} & \pm\mathbf{m}_{[110]} & \mathbf{E} & \mathbf{D}^{z}_{\bar{1}80} & \pm\mathbf{m}_{[\bar{1}10]} & \mathbf{D}^{z}_{\bar{2}70} \\
0 & 0 & \pm\mathbf{m}_{x} & \pm\mathbf{m}_{y} & \mathbf{D}^{z}_{\bar{2}70} & \pm\mathbf{m}_{[\bar{1}10]} & \mathbf{D}^{z}_{\bar{1}80} & \mathbf{E} & \pm\mathbf{m}_{[110]} & \mathbf{D}^{z}_{90} \\
0 & 0 & \mathbf{D}^{z}_{90} & \mathbf{D}^{z}_{\bar{2}70} & \pm\mathbf{m}_{y} & \mathbf{D}^{z}_{\bar{1}80} & \pm\mathbf{m}_{[\bar{1}10]} & \pm\mathbf{m}_{[110]} & \mathbf{E} & \pm\mathbf{m}_{x} \\
0 & 0 & \pm\mathbf{m}_{[\bar{1}10]} & \pm\mathbf{m}_{[110]} & \mathbf{D}^{z}_{\bar{1}80} & \pm\mathbf{m}_{y} & \mathbf{D}^{z}_{90} & \mathbf{D}^{z}_{\bar{2}70} & \pm\mathbf{m}_{x} & \mathbf{E}
\end{pmatrix}$$

with the abbreviations

$$\begin{aligned}
\mathbf{\Sigma}_1^{+} &= \mathbf{E} + \mathbf{D}^{z}_{90} + \mathbf{D}^{z}_{\bar{1}80} + \mathbf{D}^{z}_{\bar{2}70} + \mathbf{m}_{x} + \mathbf{m}_{y} + \mathbf{m}_{[110]} + \mathbf{m}_{[\bar{1}10]} \\
&= \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 8 \end{pmatrix}, \\
\mathbf{\Sigma}_1^{-} &= \mathbf{E} + \mathbf{D}^{z}_{90} + \mathbf{D}^{z}_{\bar{1}80} + \mathbf{D}^{z}_{\bar{2}70} - \mathbf{m}_{x} - \mathbf{m}_{y} - \mathbf{m}_{[110]} - \mathbf{m}_{[\bar{1}10]} \\
&= \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} = \mathbf{0}.
\end{aligned}$$

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 $\mathbf{x}_1, \mathbf{y}_1, \mathbf{z}_1, \mathbf{x}_2, \mathbf{y}_2, \mathbf{z}_2, \ldots, \mathbf{x}_{10}, \mathbf{y}_{10}, \mathbf{z}_{10}$ 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):

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

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:

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

(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 $\mathbf{x}_5$:

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

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:

$$\mathbf{P}_{11}^{(3^\pm)}(\mathbf{0}) = \frac{1}{8}\begin{pmatrix}
\boldsymbol{\Sigma}_3^\pm & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & \boldsymbol{\Sigma}_3^\pm & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & \mathbf{E} & \mathbf{D}_{180}^z & \mp\mathbf{m}_{[110]} & -\mathbf{D}_{90}^z & \pm\mathbf{m}_y & \pm\mathbf{m}_x & -\mathbf{D}_{270}^z & \mp\mathbf{m}_{[\bar{1}10]} \\
0 & 0 & \mathbf{D}_{180}^z & \mathbf{E} & \mp\mathbf{m}_{[\bar{1}10]} & -\mathbf{D}_{270}^z & \pm\mathbf{m}_x & \pm\mathbf{m}_y & -\mathbf{D}_{90}^z & \mp\mathbf{m}_{[110]} \\
0 & 0 & \mp\mathbf{m}_{[110]} & \mp\mathbf{m}_{[\bar{1}10]} & \mathbf{E} & \pm\mathbf{m}_x & -\mathbf{D}_{270}^z & -\mathbf{D}_{90}^z & \pm\mathbf{m}_y & \mathbf{D}_{180}^z \\
0 & 0 & -\mathbf{D}_{270}^z & -\mathbf{D}_{90}^z & \pm\mathbf{m}_x & \mathbf{E} & \mp\mathbf{m}_{[110]} & \mp\mathbf{m}_{[\bar{1}10]} & \mathbf{D}_{180}^z & \pm\mathbf{m}_y \\
0 & 0 & \pm\mathbf{m}_y & \pm\mathbf{m}_x & -\mathbf{D}_{90}^z & \mp\mathbf{m}_{[110]} & \mathbf{E} & \mathbf{D}_{180}^z & \mp\mathbf{m}_{[\bar{1}10]} & -\mathbf{D}_{270}^z \\
0 & 0 & \pm\mathbf{m}_x & \pm\mathbf{m}_y & -\mathbf{D}_{270}^z & \mp\mathbf{m}_{[\bar{1}10]} & \mathbf{D}_{180}^z & \mathbf{E} & \mp\mathbf{m}_{[110]} & -\mathbf{D}_{90}^z \\
0 & 0 & -\mathbf{D}_{90}^z & -\mathbf{D}_{270}^z & \pm\mathbf{m}_y & \mathbf{D}_{180}^z & \mp\mathbf{m}_{[\bar{1}10]} & \mp\mathbf{m}_{[110]} & \mathbf{E} & \pm\mathbf{m}_x \\
0 & 0 & \mp\mathbf{m}_{[\bar{1}10]} & \mp\mathbf{m}_{[110]} & \mathbf{D}_{180}^z & \pm\mathbf{m}_y & -\mathbf{D}_{90}^z & -\mathbf{D}_{270}^z & \pm\mathbf{m}_x & \mathbf{E}
\end{pmatrix}$$

with

$$\boldsymbol{\Sigma}_3^\pm = \mathbf{E} - \mathbf{D}_{90}^z + \mathbf{D}_{180}^z - \mathbf{D}_{270}^z \pm \mathbf{m}_x \pm \mathbf{m}_y \mp \mathbf{m}_{[110]} \mp \mathbf{m}_{[\bar{1}10]} = \mathbf{0}.$$

Both representations appear three times in the decomposition of the **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 $\mathbf{x}_5$:

$$\begin{aligned}
E(\mathbf{0}, 3^\pm11) &= \mathbf{P}_{11}^{(3^+)}(\mathbf{0})\,\mathbf{x}_3 \\
&= \tfrac{1}{8}[\mathbf{x}_3 - \mathbf{x}_4 \pm \mathbf{y}_5 + \mathbf{y}_6 \pm \mathbf{x}_7 \mp \mathbf{x}_8 - \mathbf{y}_9 \mp \mathbf{y}_{10}] \\
E(\mathbf{0}, 3^\pm21) &= \mathbf{P}_{11}^{(3^+)}(\mathbf{0})\,\mathbf{z}_3 \\
&= \tfrac{1}{8}[\mathbf{z}_3 + \mathbf{z}_4 \mp \mathbf{z}_5 - \mathbf{z}_6 \pm \mathbf{z}_7 \pm \mathbf{z}_8 - \mathbf{z}_9 \mp \mathbf{z}_{10}] \\
E(\mathbf{0}, 3^\pm11) &= \mathbf{P}_{11}^{(3^+)}(\mathbf{0})\,\mathbf{x}_5 \\
&= \tfrac{1}{8}[\pm\mathbf{y}_3 \mp \mathbf{y}_4 + \mathbf{x}_5 \mp \mathbf{x}_6 - \mathbf{y}_7 + \mathbf{y}_8 \pm \mathbf{x}_9 - \mathbf{x}_{10}].
\end{aligned}$$

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 $\boldsymbol{\tau}^{(2)}$ is two-dimensional and appears eight times in the decomposition of the **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:

$$\mathbf{P}_{\substack{11\\22}}^{(2)}(\mathbf{0}) = \frac{1}{4}\begin{pmatrix}
\boldsymbol{\Sigma}_2^\pm & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & \boldsymbol{\Sigma}_2^\pm & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & \mathbf{E} & -\mathbf{D}_{180}^z & 0 & \pm i\mathbf{D}_{90}^z & 0 & 0 & \mp i\mathbf{D}_{270}^z & 0 \\
0 & 0 & -\mathbf{D}_{180}^z & \mathbf{E} & 0 & \mp i\mathbf{D}_{270}^z & 0 & 0 & \pm i\mathbf{D}_{90}^z & 0 \\
0 & 0 & 0 & 0 & \mathbf{E} & 0 & \mp i\mathbf{D}_{270}^z & \pm i\mathbf{D}_{90}^z & 0 & -\mathbf{D}_{180}^z \\
0 & 0 & \mp i\mathbf{D}_{270}^z & \pm i\mathbf{D}_{90}^z & 0 & \mathbf{E} & 0 & 0 & -\mathbf{D}_{180}^z & 0 \\
0 & 0 & 0 & 0 & \pm i\mathbf{D}_{90}^z & 0 & \mathbf{E} & -\mathbf{D}_{180}^z & 0 & \mp i\mathbf{D}_{270}^z \\
0 & 0 & 0 & 0 & \mp i\mathbf{D}_{270}^z & 0 & -\mathbf{D}_{180}^z & \mathbf{E} & 0 & \pm i\mathbf{D}_{90}^z \\
0 & 0 & \pm i\mathbf{D}_{90}^z & \mp i\mathbf{D}_{270}^z & 0 & -\mathbf{D}_{180}^z & 0 & 0 & \mathbf{E} & 0 \\
0 & 0 & 0 & 0 & -\mathbf{D}_{180}^z & 0 & \pm i\mathbf{D}_{90}^z & \mp i\mathbf{D}_{270}^z & 0 & \mathbf{E}
\end{pmatrix}$$

and

$$\mathbf{P}_{\substack{12\\21}}^{(2)}(\mathbf{0}) = \frac{1}{4}\begin{pmatrix}
\boldsymbol{\Delta}_2^\pm & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & \boldsymbol{\Delta}_2^\pm & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \pm i\mathbf{m}_{[110]} & 0 & -\mathbf{m}_y & \mathbf{m}_x & 0 & \mp i\mathbf{m}_{[\bar{1}10]} \\
0 & 0 & 0 & 0 & \mp i\mathbf{m}_{[\bar{1}10]} & 0 & \mathbf{m}_x & -\mathbf{m}_y & 0 & \pm i\mathbf{m}_{[110]} \\
0 & 0 & \pm i\mathbf{m}_{[110]} & \mp i\mathbf{m}_{[\bar{1}10]} & 0 & \mathbf{m}_x & 0 & 0 & -\mathbf{m}_y & 0 \\
0 & 0 & 0 & 0 & \mathbf{m}_x & 0 & \pm i\mathbf{m}_{[110]} & \mp i\mathbf{m}_{[\bar{1}10]} & 0 & -\mathbf{m}_y \\
0 & 0 & -\mathbf{m}_y & \mathbf{m}_x & 0 & \pm i\mathbf{m}_{[110]} & 0 & 0 & \mp i\mathbf{m}_{[\bar{1}10]} & 0 \\
0 & 0 & \mathbf{m}_x & -\mathbf{m}_y & 0 & \mp i\mathbf{m}_{[\bar{1}10]} & 0 & 0 & \pm i\mathbf{m}_{[110]} & 0 \\
0 & 0 & 0 & 0 & -\mathbf{m}_y & 0 & \mp i\mathbf{m}_{[\bar{1}10]} & \pm i\mathbf{m}_{[110]} & 0 & \mathbf{m}_x \\
0 & 0 & \mp i\mathbf{m}_{[\bar{1}10]} & \pm i\mathbf{m}_{[110]} & 0 & -\mathbf{m}_y & 0 & 0 & \mathbf{m}_x & 0
\end{pmatrix}$$

with

$$\mathbf{\Sigma}_2^{\pm} = \mathbf{E} \pm i\mathbf{D}_{90}^z - \mathbf{D}_{180}^z \mp i\mathbf{D}_{270}^z = \begin{pmatrix} 2 & \mp 2i & 0 \\ \pm 2i & 2 & 0 \\ 0 & 0 & 0 \end{pmatrix},$$

$$\mathbf{\Delta}_2^{\pm} = \mathbf{m}_x - \mathbf{m}_y \pm i\mathbf{m}_{[110]} \mp i\mathbf{m}_{[\bar{1}10]} = \begin{pmatrix} -2 & \mp 2i & 0 \\ \mp 2i & 2 & 0 \\ 0 & 0 & 0 \end{pmatrix}.$$

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

$$\mathbf{E}(\mathbf{0}, 211) = \mathbf{P}_{11}^{(2)}(\mathbf{0})\,\mathbf{x}_1 = \tfrac{1}{2}[\mathbf{x}_1 + i\mathbf{y}_1]$$
$$\mathbf{E}(\mathbf{0}, 221) = \mathbf{P}_{11}^{(2)}(\mathbf{0})\,\mathbf{x}_2 = \tfrac{1}{2}[\mathbf{x}_2 + i\mathbf{y}_2]$$
$$\mathbf{E}(\mathbf{0}, 231) = \mathbf{P}_{11}^{(2)}(\mathbf{0})\,\mathbf{x}_3 = \tfrac{1}{4}[\mathbf{x}_3 + \mathbf{x}_4 + i\mathbf{y}_6 + i\mathbf{y}_9]$$
$$\mathbf{E}(\mathbf{0}, 241) = \mathbf{P}_{11}^{(2)}(\mathbf{0})\,\mathbf{x}_5 = \tfrac{1}{4}[\mathbf{x}_5 + \mathbf{x}_{10} + i\mathbf{y}_7 + i\mathbf{y}_8]$$
$$\mathbf{E}(\mathbf{0}, 251) = \mathbf{P}_{11}^{(2)}(\mathbf{0})\,\mathbf{x}_6 = \tfrac{1}{4}[\mathbf{x}_6 + \mathbf{x}_9 + i\mathbf{y}_3 + i\mathbf{y}_4]$$
$$\mathbf{E}(\mathbf{0}, 261) = \mathbf{P}_{11}^{(2)}(\mathbf{0})\,\mathbf{x}_7 = \tfrac{1}{4}[\mathbf{x}_7 + \mathbf{x}_8 + i\mathbf{y}_5 + i\mathbf{y}_{10}]$$
$$\mathbf{E}(\mathbf{0}, 271) = \mathbf{P}_{11}^{(2)}(\mathbf{0})\,\mathbf{z}_3 = \tfrac{1}{4}[\mathbf{z}_3 - \mathbf{z}_4 - i\mathbf{z}_6 + i\mathbf{z}_9]$$
$$\mathbf{E}(\mathbf{0}, 281) = \mathbf{P}_{11}^{(2)}(\mathbf{0})\,\mathbf{z}_5 = \tfrac{1}{4}[\mathbf{z}_5 - \mathbf{z}_{10} + i\mathbf{z}_7 - i\mathbf{z}_8]$$

$$\mathbf{E}(\mathbf{0}, 212) = \mathbf{P}_{21}^{(2)}(\mathbf{0})\,\mathbf{x}_1 = \tfrac{1}{2}[-\mathbf{x}_1 + i\mathbf{y}_1]$$
$$\mathbf{E}(\mathbf{0}, 222) = \mathbf{P}_{21}^{(2)}(\mathbf{0})\,\mathbf{x}_2 = \tfrac{1}{2}[-\mathbf{x}_2 + i\mathbf{y}_2]$$
$$\mathbf{E}(\mathbf{0}, 232) = \mathbf{P}_{21}^{(2)}(\mathbf{0})\,\mathbf{x}_3 = \tfrac{1}{4}[-\mathbf{x}_7 - \mathbf{x}_8 + i\mathbf{y}_5 + i\mathbf{y}_{10}]$$
$$\mathbf{E}(\mathbf{0}, 242) = \mathbf{P}_{21}^{(2)}(\mathbf{0})\,\mathbf{x}_5 = \tfrac{1}{4}[-\mathbf{x}_6 - \mathbf{x}_9 + i\mathbf{y}_3 + i\mathbf{y}_4]$$
$$\mathbf{E}(\mathbf{0}, 252) = \mathbf{P}_{21}^{(2)}(\mathbf{0})\,\mathbf{x}_6 = \tfrac{1}{4}[-\mathbf{x}_5 - \mathbf{x}_{10} + i\mathbf{y}_7 + i\mathbf{y}_8]$$
$$\mathbf{E}(\mathbf{0}, 262) = \mathbf{P}_{21}^{(2)}(\mathbf{0})\,\mathbf{x}_7 = \tfrac{1}{4}[-\mathbf{x}_3 - \mathbf{x}_4 + i\mathbf{y}_6 + i\mathbf{y}_9]$$
$$\mathbf{E}(\mathbf{0}, 272) = \mathbf{P}_{21}^{(2)}(\mathbf{0})\,\mathbf{z}_3 = \tfrac{1}{4}[-\mathbf{z}_7 + \mathbf{z}_8 - i\mathbf{z}_5 + i\mathbf{z}_{10}]$$
$$\mathbf{E}(\mathbf{0}, 282) = \mathbf{P}_{21}^{(2)}(\mathbf{0})\,\mathbf{z}_5 = \tfrac{1}{4}[\mathbf{z}_6 - \mathbf{z}_9 - i\mathbf{z}_3 + i\mathbf{z}_4].$$

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 vibrations: *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 $\mathbf{e}(\mathbf{q}, sa\lambda)$, $\lambda = 1, \ldots, f_s$, but also

$$\overline{\mathbf{e}}(\mathbf{q}, sa\lambda) = \mathbf{T}(\mathbf{q}, \mathbf{A})\,\mathbf{e}(\mathbf{q}, sa\lambda) \qquad (2.1.3.59)$$

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, $\mathbf{T}(\mathbf{q}, \mathbf{A})\,\mathbf{e}(\mathbf{q}, sa\lambda)$ is orthogonal to all vectors $\mathbf{e}(\mathbf{q}, sa\lambda')$, it belongs to another vector space corresponding to different indices s' and a'. In this case, the eigenfrequencies $\omega_{\mathbf{q},sa}$

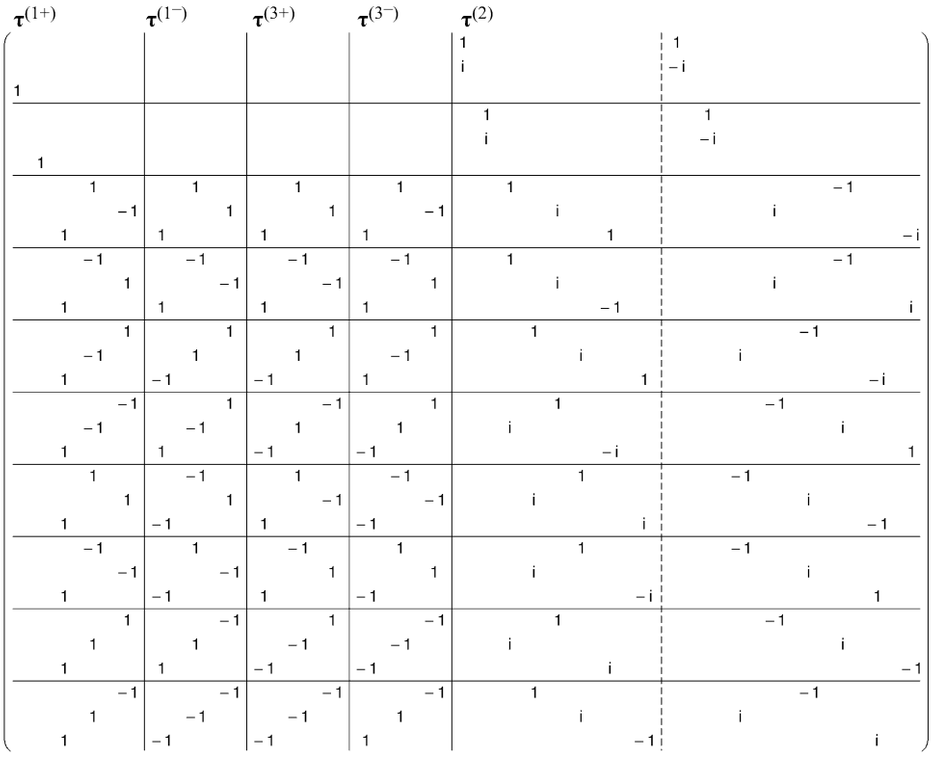

Fig. 2.1.3.7. Matrix of symmetry coordinates at $\mathbf{q} = \mathbf{0}$ for the example structure given in Fig. 2.1.3.4 and Table 2.1.3.1.

and $\omega_{\mathbf{q},s'a'}$ 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 $\overline{\mathbf{e}}(\mathbf{q}, sa\lambda)$. According to the multiplication rule for the **T**-matrix operators, (2.1.3.32), we obtain

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

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 $\boldsymbol{\tau}^{(s)}(\mathbf{q},\mathbf{R})$:

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

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

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

A being an arbitrary representative of those symmetry operations that invert the wavevector **q**.

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

If, on the other hand, the two representations are equivalent, there is a matrix $\boldsymbol{\beta}$ with

$$\overline{\boldsymbol{\tau}^{(s)}}(\mathbf{q},\mathbf{R}) = \boldsymbol{\beta}^{-1}\,\boldsymbol{\tau}^{(s)}(\mathbf{q},\mathbf{R})\,\boldsymbol{\beta} \tag{2.1.3.63}$$

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

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

In many cases, **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* [$\boldsymbol{\beta}\boldsymbol{\beta}^* = +\varphi(\mathbf{q},\mathbf{A},\mathbf{A})\boldsymbol{\tau}^{(s)}(\mathbf{q},\mathbf{A}^2)$] and those that correspond to the − sign

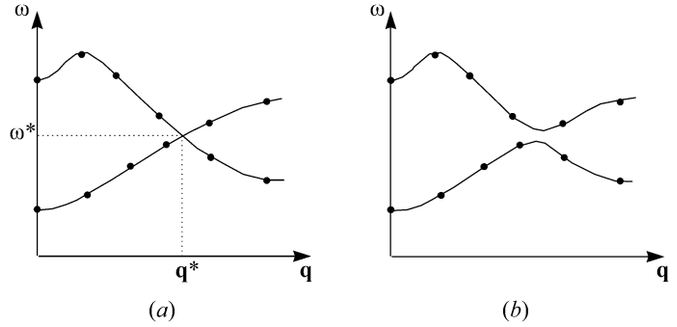

Fig. 2.1.3.8. (*a*) Accidental degeneracy of phonons with different symmetry. (*b*) Anticrossing of phonons with the same symmetry (no degeneracy).

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 $\overline{\mathbf{e}}(\mathbf{q}, sa\lambda)$ 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 $\overline{\boldsymbol{\tau}^{(s)}}(\mathbf{q}, \mathbf{R}) = \boldsymbol{\tau}^{(s)*}(\mathbf{q}, \mathbf{R})$. In this case, representations are of the first kind if they are real representations.

For representations of the second kind, $\overline{\mathbf{e}}(\mathbf{q}, sa\lambda)$ 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:

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

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:

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

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 $\omega^2_{\mathbf{q},sa}$ 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^z_{120} and D^z_{240}. 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:

$$\mathbf{m}_z\,\mathbf{D}^z_{120}\,\mathbf{m}_z = \mathbf{D}^z_{120}$$
$$\mathbf{m}_z\,\mathbf{D}^z_{240}\,\mathbf{m}_z = \mathbf{D}^z_{240}.$$

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

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

Obviously, $\bar{\tau}^{(2)}$ and $\tau^{(2)}$ are inequivalent and, hence, pairs of phonons corresponding to representations $\tau^{(2)}$ and $\tau^{(3)}$, 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, $\tau^{(2)}(\mathbf{0})$ and $\tau^{(6)}(\mathbf{0})$ form a pair of complex-conjugated representations as well as $\tau^{(3)}(\mathbf{0})$ and $\tau^{(5)}(\mathbf{0})$. Therefore, always two lattice vibrations of these symmetries exhibit the same frequencies. The eigenvectors for representation $\tau^{(6)}(\mathbf{0})$ or $\tau^{(5)}(\mathbf{0})$ can be combined with the eigenvectors of corresponding modes of representations $\tau^{(2)}(\mathbf{0})$ or $\tau^{(3)}(\mathbf{0})$, 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^z_{120}, D^z_{240}) this factor is unity, whereas it equals the complex unit i for the other elements of the point group (D^z_{60}, D^z_{180}, D^z_{300}). 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: $\tau^{(1)}(\mathbf{c}^*/2)$ and $\tau^{(4)}(\mathbf{c}^*/2)$; $\tau^{(2)}(\mathbf{c}^*/2)$ and $\tau^{(3)}(\mathbf{c}^*/2)$; and $\tau^{(5)}(\mathbf{c}^*/2)$ and $\tau^{(6)}(\mathbf{c}^*/2)$. 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 $\tau^{(i)}$. T and E are reserved for representations that (at the Γ point) are triply and doubly degenerate, respectively. An index ± 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^z_{120}	D^z_{240}
$\tau^{(1)}$	1	1	1
$\tau^{(2)}$	1	$\exp(i2\pi/3)$	$\exp(-i2\pi/3)$
$\tau^{(3)}$	1	$\exp(-i2\pi/3)$	$\exp(i2\pi/3)$

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^z_{60}	D^z_{120}	D^z_{180}	D^z_{240}	D^z_{300}
$\tau^{(1)}(\mathbf{0})$	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^z_{60}	D^z_{120}	D^z_{180}	D^z_{240}	D^z_{300}
$\tau^{(1)}(\mathbf{c}^*/2)$	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^z_{180}. Therefore, the irreducible representations of Fig. 2.1.3.9 can be identified as $\mathrm{A} = \tau^{(1)}$, $\mathrm{B} = \tau^{(2)}$, $\mathrm{E}_1^- = \tau^{(2)}$, $E_1^+ = \tau^{(6)}$, $E_1^+ = \tau^{(5)}$ 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 $G_o(\mathbf{q}_{\mathrm{BZ}})$, where $\mathbf{q}_{\mathrm{BZ}}$ represents a wavevector at the Brillouin-zone boundary in the direction of $\mathbf{q}$. When leaving a prominent wavevector ($\mathbf{q} = \mathbf{0}$ or $\mathbf{q} = \mathbf{q}_{\mathrm{BZ}}$), 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

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

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 $\boldsymbol{\tau}^{(s)}(\mathbf{q})$. The multiplicities are given by the characters using the following equation:

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

or (2.1.3.68)

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

Hence, phonons corresponding to irreducible representations $\boldsymbol{\tau}^{(s)}(\mathbf{q})$ 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.

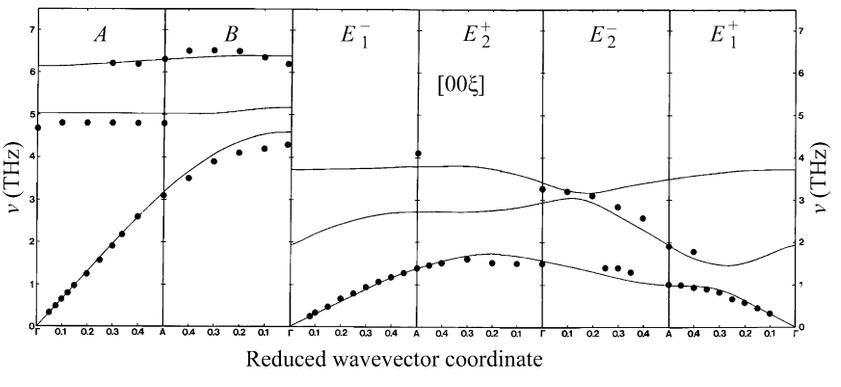

Fig. 2.1.3.9. Low-frequency part of the phonon dispersion of $KLiSO_4$ at room temperature (space group $P6_3$). The phonons are arranged in an extended zone scheme according to the different irreducible representations [after Eckold & Hahn (1987)]. The symbols represent experimental data and the lines 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 $G_o(\mathbf{q}) = \{\mathbf{E}, \mathbf{m}_y\}$ and there are two irreducible representations, a symmetric one (with respect to m_y) $\boldsymbol{\tau}^+(\mathbf{q})$ with $\boldsymbol{\tau}^+(\mathbf{q}, \mathbf{m}_y) = 1$ and an antisymmetric one with $\boldsymbol{\tau}^-(\mathbf{q}, \mathbf{m}_y) = -1$. 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

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

	Symmetry operation							
P4mm	E	D^z_{90}	D^z_{180}	D^z_{270}	m_x	m_y	$m_{[\bar{1}10]}$	$m_{[110]}$
$\tau^{(1+)}(\mathbf{0})$	**1**	1	1	1	1	**1**	1	1
$\tau^{(1-)}(\mathbf{0})$	**1**	1	1	1	−1	**−1**	−1	−1
$\tau^{(3+)}(\mathbf{0})$	**1**	−1	1	−1	1	**1**	−1	−1
$\tau^{(3-)}(\mathbf{0})$	**1**	−1	1	−1	−1	**−1**	1	1
$\boldsymbol{\tau}^{(2)}(\mathbf{0})$	$\begin{pmatrix}\mathbf{1} & \mathbf{0}\\ \mathbf{0} & \mathbf{1}\end{pmatrix}$	$\begin{pmatrix}i & 0\\ 0 & -i\end{pmatrix}$	$\begin{pmatrix}-1 & 0\\ 0 & -1\end{pmatrix}$	$\begin{pmatrix}-i & 0\\ 0 & i\end{pmatrix}$	$\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}$	$\begin{pmatrix}\mathbf{0} & \mathbf{-1}\\ \mathbf{-1} & \mathbf{0}\end{pmatrix}$	$\begin{pmatrix}0 & -i\\ i & 0\end{pmatrix}$	$\begin{pmatrix}0 & i\\ -i & 0\end{pmatrix}$
$\chi_{\boldsymbol{\tau}^{(2)}(\mathbf{0})}$	**2**	0	−2	0	0	**0**	0	0

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

The two-dimensional representation $\boldsymbol{\tau}^{(2)}(\mathbf{0})$ exhibits the character $\chi_{\boldsymbol{\tau}^{(2)}(\mathbf{0},\mathbf{m}_y)} = 0$. 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.

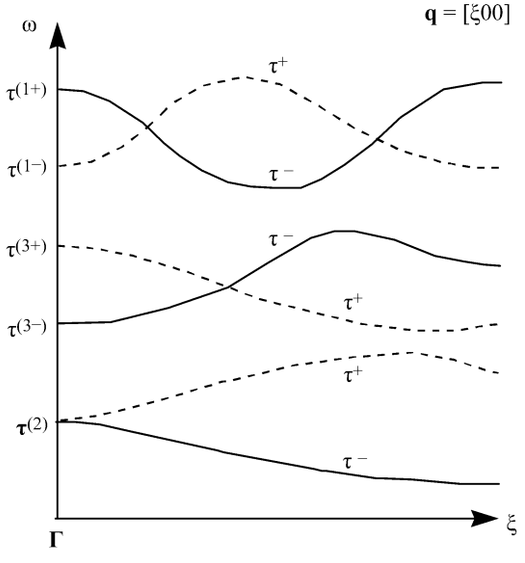

Fig. 2.1.3.10. Illustration of the compatibility relations for phonons in a tetragonal crystal with space group *P4mm* for wavevectors along [ξ00].

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 $\boldsymbol{\tau}_v$ 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 $\boldsymbol{\tau}$ within the decomposition of the vector representation $\boldsymbol{\tau}_v$ can be calculated from the respective characters $\chi_{\boldsymbol{\tau}}$ and $\chi_{\boldsymbol{\tau}_v}$. Hence we may formulate the criterion for infrared activity as follows: Phonons corresponding to an irreducible representation $\boldsymbol{\tau}$ are infrared active if

$$c_{\boldsymbol{\tau}} = (1/|G|) \sum_{\mathbf{R}} \chi_{\boldsymbol{\tau}}(\mathbf{R})\, \chi_{\boldsymbol{\tau}_v}(\mathbf{R}) \neq 0. \qquad (2.1.3.69)$$

(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

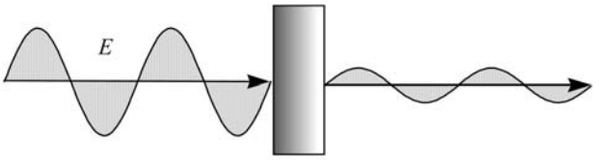

Fig. 2.1.3.11. Principle of infrared absorption.

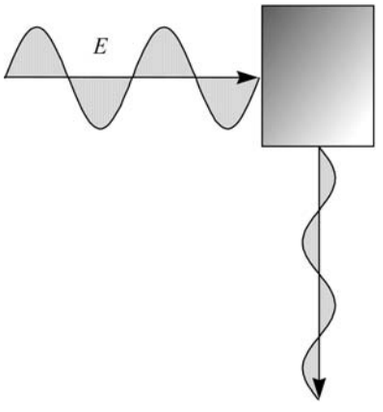

Fig. 2.1.3.12. Principle of Raman spectroscopy.

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

	Symmetry operation							
P4mm	E	D^z_{90}	D^z_{180}	D^z_{270}	m_x	m_y	$m_{[\bar{1}10]}$	$m_{[110]}$
$\chi_{\tau^{(1^+)}}$	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
$\boldsymbol{\tau}_v$	$\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix}$	$\begin{pmatrix}0&-1&0\\1&0&0\\0&0&1\end{pmatrix}$	$\begin{pmatrix}-1&0&0\\0&-1&0\\0&0&1\end{pmatrix}$	$\begin{pmatrix}0&1&0\\-1&0&0\\0&0&1\end{pmatrix}$	$\begin{pmatrix}-1&0&0\\0&1&0\\0&0&1\end{pmatrix}$	$\begin{pmatrix}1&0&0\\0&-1&0\\0&0&1\end{pmatrix}$	$\begin{pmatrix}0&1&0\\1&0&0\\0&0&1\end{pmatrix}$	$\begin{pmatrix}0&-1&0\\-1&0&0\\0&0&1\end{pmatrix}$
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 $\boldsymbol{\tau}_T$. 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 $\boldsymbol{\tau}$ are Raman active if

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

Without going into details, we note that the tensor representation $\boldsymbol{\tau}_T$ is the symmetric square of the vector representation $\boldsymbol{\tau}_v$ and its character may be calculated from the character of $\boldsymbol{\tau}_v$,

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

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 $\boldsymbol{\tau}^{(2)}$, 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:

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

Hence phonons corresponding to the representations $\tau^{(1^+)}$, $\tau^{(3^+)}$, $\tau^{(3^-)}$ and $\boldsymbol{\tau}^{(2)}$ 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 $\mathbf{S}_- \circ G_o(\mathbf{q})$
$\mathbf{C}(\mathbf{q}) = (C^{\alpha\beta}_{\kappa\kappa'}(\mathbf{q}))$	modified dynamical matrix
c_{ij}	elastic stiffness in Voigt notation
(c_{jklm})	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
$\mathbf{D}(\mathbf{q}) = (D^{\alpha\beta}_{\kappa\kappa'}(\mathbf{q}))$	dynamical matrix
$\overline{\mathbf{D}}^{(s)}(\mathbf{q})$	submatrix of the block-diagonalized dynamical matrix corresponding to irreducible multiplier representation σ