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

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

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