

2.1. PHONONS

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

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

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

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

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

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

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

2.1.3.7.1. Example

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

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

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

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

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

2.1.4. Conclusion

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

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

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

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

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

2.1.5. Glossary

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

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

References

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