International Tables for Crystallography (2006). Vol. D, Section 2.1.4, p. 291.

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 $\chi_{\boldsymbol{\tau}}$ and $\chi_{\boldsymbol{\tau}_v}$: Phonons corresponding to an irreducible representation $\boldsymbol{\tau}$ are Raman active if

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

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 $\boldsymbol{\tau}_v$,

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

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