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.

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

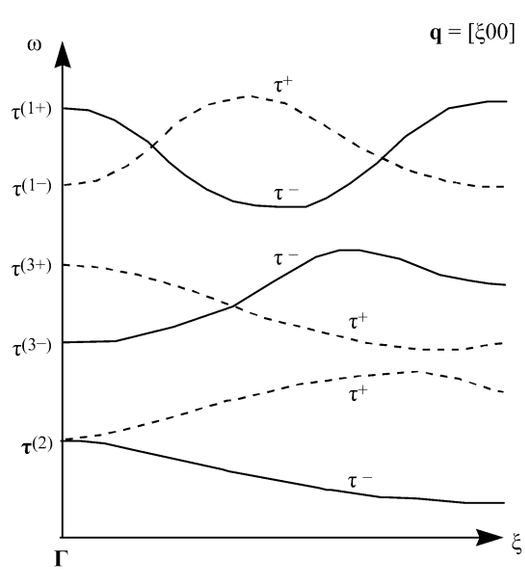

Fig. 2.1.3.10. Illustration of the compatibility relations for phonons in a tetragonal crystal with space group *P4mm* for wavevectors along [ξ00].

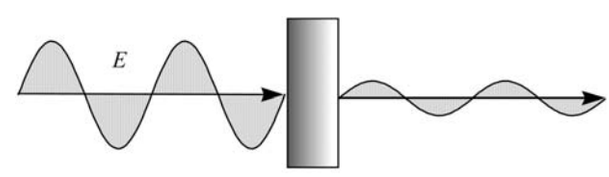

Fig. 2.1.3.11. Principle of infrared absorption.

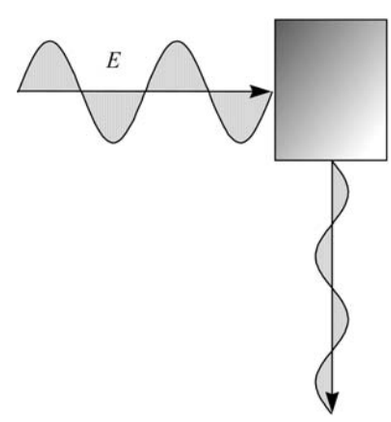

Fig. 2.1.3.12. Principle of Raman spectroscopy.