4 Dynamics of Atoms in Crystals

The physical properties of a solid can be roughly divided into those that are determined by the electrons and those that relate to the movement of the atoms about their equilibrium positions. In the latter category are, for example, the sound velocity and also the thermal properties: specific heat, thermal expansion, and – for semiconductors and insulators – the thermal conductivity. The hardness of a material is also determined, in principle, by the movement of the atoms about their equilibrium positions. Here, however, structural defects generally play a decisive role.

The division of solid properties into atom dynamics and electronic properties is qualitatively easy to justify: the motions of atomic nuclei are, due to their high mass, much slower than the motions of the electrons. If the atoms are displaced from their equilibrium positions, then the electrons adopt a new distribution (with higher total energy). The electron system, however, remains thereby in a ground state. If the initial positions of the nuclei are restored, then the energy expended is recovered in full and there remains no excitation of the electron system. The total energy as a function of the coordinates of all atomic nuclei thus plays the role of a potential for the atomic motion. This approach is, of course, only an approximation. There are also effects for which the interaction between the atom dynamics and the electron system become significant (Chap. 9). The so-called "adiabatic" approximation to be discussed here was introduced by Born and Oppenheimer [4.1].

Since the potential for the motion of the atomic nuclei is given by the total energy and thus, in essence, by the properties of the electron system, one might try initially to describe all the details of the electronic properties and derive from these the potential for the atomic motion. Finally, one could deduce from this all those properties of the solid that are determined by the atomic motion. This approach is indeed possible, but for our purposes in this text book it involves excessive mathematical effort. Fortunately, it is possible to obtain many important predictions about the thermal behavior of solids and their interaction with electromagnetic radiation without needing to know the explicit form of the potential for atomic motion. One simply needs a general formalism which enables equations of motion to be formulated and solved for an arbitrary potential. We will deal with such a formalism in the following sections. The concepts presented here will be a

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necessary prerequisite for an understanding of Chap. 5 in which we discuss the thermal properties of solids.

4.1 The Potential

First of all we require a suitable indexing system to refer to the individual atoms. Unfortunately, this is rather complicated due to the many degrees of freedom present. As in the past, we number the unit cells by the triplets $\boldsymbol{n} = (n_1, n_2, n_3)$ or $\boldsymbol{m} = (m_1, m_2, m_3)$ and the atoms within each cell by α, β. The ith component of the equilibrium position vector of an atom is then denoted by $r_{\boldsymbol{n}\alpha i}$ and the displacement from the equilibrium position by $u_{\boldsymbol{n}\alpha i}$ (Fig. 4.1). We now expand the total energy of the crystal Φ, which is a function of all nuclear coordinates, in a Taylor series about the equilibrium positions $r_{\boldsymbol{n}\alpha i}$

$$\Phi\,(r_{\boldsymbol{n}\alpha i} + u_{\boldsymbol{n}\alpha i}) = \Phi(r_{\boldsymbol{n}\alpha i}) + \frac{1}{2}\sum_{\substack{\boldsymbol{n}\alpha i\\ \boldsymbol{m}\beta j}} \frac{\partial^2 \Phi}{\partial r_{\boldsymbol{n}\alpha i}\,\partial r_{\boldsymbol{m}\beta j}}\, u_{\boldsymbol{n}\alpha i} u_{\boldsymbol{m}\beta j} \dots \,. \tag{4.1}$$

The terms that are linear in $u_{\boldsymbol{n}\alpha i}$ disappear since the expansion is about the equilibrium (minimum energy) position. The summation indices $\boldsymbol{n}, \boldsymbol{m}$ run

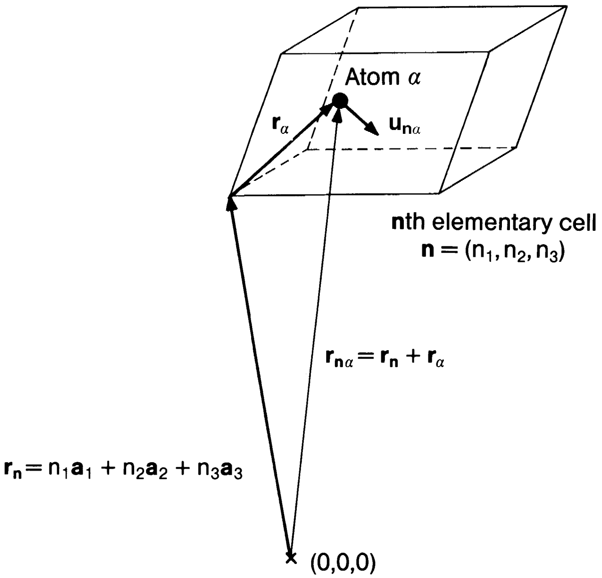


Fig. 4.1. Explanation of the vector nomenclature used to describe lattice vibrations in a three-dimensional periodic crystal: The lattice vector $\boldsymbol{r}_{\boldsymbol{n}}$ extends from an arbitrarily chosen lattice point $(0,0,0)$ to the origin of the $\boldsymbol{n}$th unit cell $\boldsymbol{n} = (n_1, n_2, n_3)$, from which the positions of the atoms α are described by the vector $\boldsymbol{r}_\alpha$. The displacement from equilibrium of atom α in cell n is then $\boldsymbol{u}_{\boldsymbol{n}\alpha}$. Thus the time-dependent position of this atom relative to $(0,0,0)$ is $\boldsymbol{r}_{\boldsymbol{n}\alpha} + \boldsymbol{u}_{\boldsymbol{n}\alpha}(t)$ where $\boldsymbol{r}_{\boldsymbol{n}\alpha} = \boldsymbol{r}_{\boldsymbol{n}} + \boldsymbol{r}_\alpha$

over all unit cells; α,β over the atoms in the cell; and i,j over the three spatial coordinate directions. Higher terms in the expansion will be neglected for the time being. Equation (4.1) then represents an extension of the harmonic oscillator potential to the case of many particles. The neglect of the higher order terms in (4.1) is therefore known as the "harmonic" approximation. Effects that can only be described by the inclusion of additional terms (e.g., the thermal expansion of solids; Chap. 5) are referred to as anharmonic effects.

The derivatives of the potential

$$\frac{\partial^2 \Phi}{\partial r_{\boldsymbol{n}\alpha i}\,\partial r_{\boldsymbol{m}\beta j}} = \Phi_{\boldsymbol{n}\alpha i}^{\boldsymbol{m}\beta j} \tag{4.2}$$

are called "coupling constants". They have the dimensions of spring constants and serve to generalize the spring constants of the harmonic oscillator to a system with many degrees of freedom. The quantity $-\Phi_{\boldsymbol{n}\alpha i}^{\boldsymbol{m}\beta j} u_{\boldsymbol{m}\beta j}$ is thus the force exerted on atom α in the unit cell $\boldsymbol{n}$ in the i-direction when the atom β in unit cell $\boldsymbol{m}$ is displaced by a distance $u_{\boldsymbol{m}\beta j}$ in the j-direction. For positive values of $\Phi_{\boldsymbol{n}\alpha i}^{\boldsymbol{m}\beta j}$ the force acts in the direction opposite to that of u. We see that this description allows for interactions between all atoms regardless of their separation from one another. In simple models, one often includes only the interaction between nearest neighbor atoms.

The coupling constants must satisfy a number of conditions that arise from the isotropy of space, the translation invariance, and the point group symmetry [2.2]. The translation invariance upon displacement of the lattice by an arbitrary lattice constant implies, for example, that the quantity $\Phi_{\boldsymbol{n}\alpha i}^{\boldsymbol{m}\beta j}$ can only depend on the difference between $\boldsymbol{m}$ and $\boldsymbol{n}$:

$$\Phi_{\boldsymbol{n}\alpha i}^{\boldsymbol{m}\beta j} = \Phi_{\boldsymbol{0}\alpha i}^{(\boldsymbol{m}-\boldsymbol{n})\beta j} \; . \tag{4.3}$$

4.2 The Equation of Motion

For the displacement u of atom α in cell $\boldsymbol{n}$ in direction i, the sum of the coupling forces and the force of inertia must be equal to zero (Newton's law):

$$M_\alpha \ddot{u}_{\boldsymbol{n}\alpha i} + \sum_{\boldsymbol{m}\beta j} \Phi_{\boldsymbol{n}\alpha i}^{\boldsymbol{m}\beta j} u_{\boldsymbol{m}\beta j} = 0 \; . \tag{4.4}$$

For N unit cells each with r atoms, this gives rise to $3rN$ differential equations which describe the motion of the atoms. Fortunately, for periodic structures, it is possible to use a suitable ansatz in order to achieve a significant decoupling. This involves writing the displacements $u_{\boldsymbol{n}\alpha i}$ in terms of a plane wave with respect to the cell coordinates:

$$u_{\boldsymbol{n}\alpha i} = \frac{1}{\sqrt{M_\alpha}} u_{\alpha i}(\boldsymbol{q}) \mathrm{e}^{\mathrm{i}(\boldsymbol{q}\cdot\boldsymbol{r}_n - \omega t)} . \tag{4.5}$$

In contrast to a normal plane wave, this wave is only defined at the lattice points $\boldsymbol{r}_{\boldsymbol{n}}$. On substitution of this form into (4.4) one obtains an equation for the amplitude $u_{\alpha i}$:

$$-\omega^2 u_{\alpha i}(\boldsymbol{q}) + \sum_{\beta j} \underbrace{\sum_{\boldsymbol{m}} \frac{1}{\sqrt{M_\alpha M_\beta}} \Phi^{\boldsymbol{m}\beta j}_{\boldsymbol{n}\alpha i} \mathrm{e}^{\mathrm{i}\,\boldsymbol{q}\cdot(\boldsymbol{r}_m - \boldsymbol{r}_n)}}_{D^{\beta j}_{\alpha i}(\boldsymbol{q})} u_{\beta j}(\boldsymbol{q}) = 0 . \tag{4.6}$$

Due to the translational invariance, the terms of the sum depend, as in (4.3), only on the difference $\boldsymbol{m}$–$\boldsymbol{n}$. After performing the summation over $\boldsymbol{m}$, one obtains a quantity $D^{\beta j}_{\alpha i}(\boldsymbol{q})$ that is independent of $\boldsymbol{n}$. It couples the amplitudes to one another in a manner that does not depend on $\boldsymbol{n}$. This justifies the fact that the amplitudes in the ansatz (4.5) were written without the index $\boldsymbol{n}$. The quantities $D^{\beta j}_{\alpha i}(\boldsymbol{q})$ form the so-called dynamical matrix. The system of equations

$$-\omega^2 u_{\alpha i}(\boldsymbol{q}) + \sum_{\beta j} D^{\beta j}_{\alpha i}(\boldsymbol{q})\, u_{\beta j}(\boldsymbol{q}) = 0 \tag{4.7}$$

is a linear homogeneous system of order $3r$. In the case of a primitive unit cell we have $r = 1$ and for every wave vector $\boldsymbol{q}$ we have a system of merely three equations to solve. This is a convincing demonstration of the simplifications brought about by the translational symmetry.

A system of linear homogeneous equations only has solutions (eigensolutions) if the determinant

$$\mathrm{Det}\,\{D^{\beta j}_{\alpha i}(\boldsymbol{q}) - \omega^2 \mathbf{1}\} = 0 \tag{4.8}$$

vanishes. This equation has exactly $3r$ different solutions, $\omega(\boldsymbol{q})$, for each $\boldsymbol{q}$. The dependence $\omega(\boldsymbol{q})$ is known as the *dispersion relation*. The $3r$ different solutions are called the *branches* of the dispersion relation. It is possible to make a number of general statements about these branches. However, rather than deriving these mathematically from (4.8) for the general case, we will discuss the special case of a diatomic linear chain. We can then make use of the results to present an overview of the dispersion branches of a three-dimensional crystal.

4.3 The Diatomic Linear Chain

The formalism developed above can be illustrated most readily in terms of the diatomic linear chain model. Although this model has little in common with a real solid, it is frequently discussed because of its simple mathematics. We consider a linear chain in which all nearest neighbors are connected by identical springs with force constant f. The unit cell contains two atoms of masses M_1 and M_2 (Fig. 4.2).

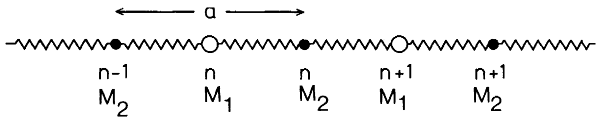


Fig. 4.2. The diatomic linear chain model

The indices α, β in (4.4) thus take on the possible values 1 and 2; the index i has only one value, since the system is one dimensional, and can therefore be omitted. Since it is assumed that only nearest neighbors interact, the index m in the sum in (4.4) can take only the values $n+1, n, n-1$. One thus obtains the following equations

$$\begin{aligned} &M_1\ddot{u}_{n1} + \Phi^{n-1,2}_{n1} u_{n-1,2} + \Phi^{n1}_{n1} u_{n1} + \Phi^{n2}_{n1} u_{n2} = 0\ , \\ &M_2\ddot{u}_{n2} + \Phi^{n1}_{n2} u_{n1} + \Phi^{n2}_{n2} u_{n2} + \Phi^{n+1,1}_{n2} u_{n+1,1} = 0\ . \end{aligned} \tag{4.9}$$

The values of these remaining coupling constants are

$$\begin{aligned} &\Phi^{n-1,2}_{n1} = \Phi^{n2}_{n1} = \Phi^{n1}_{n2} = \Phi^{n+1,1}_{n2} = -f \quad \text{and} \\ &\Phi^{n1}_{n1} = \Phi^{n2}_{n2} = +2f\ . \end{aligned} \tag{4.10}$$

Thus we obtain

$$\begin{aligned} &M_1\ddot{u}_{n1} + f(2u_{n1} - u_{n2} - u_{n-1,2}) = 0\ , \\ &M_2\ddot{u}_{n2} + f(2u_{n2} - u_{n1} - u_{n+1,1}) = 0\ . \end{aligned} \tag{4.11}$$

The plane-wave ansatz (4.5) then reads

$$u_{n\alpha} = \frac{1}{\sqrt{M_\alpha}}\, u_\alpha(q)\, \mathrm{e}^{\mathrm{i}(qan-\omega t)}\ . \tag{4.12}$$

We insert (4.12) into (4.11) to give

$$\begin{aligned} &\left(\frac{2f}{M_1} - \omega^2\right) u_1 - f\frac{1}{\sqrt{M_1 M_2}}(1 + \mathrm{e}^{-\mathrm{i}qa}) u_2 = 0\ , \\ &-f\frac{1}{\sqrt{M_1 M_2}}(1 + \mathrm{e}^{\mathrm{i}qa}) u_1 + \left(\frac{2f}{M_2} - \omega^2\right) u_2 = 0\ . \end{aligned} \tag{4.13}$$

The dynamical matrix $D^{\beta j}_{\alpha i}(\boldsymbol{q})$ is therefore

$$\begin{pmatrix} \dfrac{2f}{M_1} & \dfrac{-f}{\sqrt{M_1 M_2}}(1 + \mathrm{e}^{-\mathrm{i}qa}) \\ \dfrac{-f}{\sqrt{M_1 M_2}}(1 + \mathrm{e}^{\mathrm{i}qa}) & \dfrac{2f}{M_2} \end{pmatrix} . \tag{4.14}$$

Setting the determinant of the system (4.13) equal to zero leads to the dispersion relation

$$\omega^2 = f\left(\frac{1}{M_1}+\frac{1}{M_2}\right) \pm f\left[\left(\frac{1}{M_1}+\frac{1}{M_2}\right)^2 - \frac{4}{M_1 M_2}\sin^2\frac{qa}{2}\right]^{1/2} . \tag{4.15}$$

This dispersion relation is clearly periodic in q with a period given by

$$\begin{aligned} \frac{q\,a}{2} &= \pi \,, \\ q &= \frac{2\pi}{a} \,. \end{aligned} \tag{4.16}$$

The periodic repeat distance in q is thus exactly one reciprocal lattice vector. It can in fact be shown that this property holds for all lattices. To do so we simply need to go back to the definition of the dynamical matrix. We see that on account of (3.15)

$$D_{\alpha i}^{\beta j}(\boldsymbol{q}) = D_{\alpha i}^{\beta j}(\boldsymbol{q}+\boldsymbol{G}) \quad \text{with} \quad \boldsymbol{G}\cdot\boldsymbol{r}_n = 2\pi m \,. \tag{4.17}$$

Thus the eigensolution (4.7 or 4.8) must satisfy the condition

$$\omega(\boldsymbol{q}) = \omega(\boldsymbol{q}+\boldsymbol{G}) \,. \tag{4.18}$$

Furthermore we have

$$\omega(-\boldsymbol{q}) = \omega(\boldsymbol{q}) \,, \tag{4.19}$$

since $u(-\boldsymbol{q})$ represents a wave identical to $u(\boldsymbol{q})$ but propagating in the opposite direction. However, the forward- and backward-propagating waves are related to one another by time reversal. Since the equations of motion are invariant with respect to time reversal, it follows that the eigenfrequencies for $+\boldsymbol{q}$ and $-\boldsymbol{q}$ must be equal. It is also possible to derive the inversion symmetry of ω in $\boldsymbol{q}$-space (4.19) from the corresponding symmetry of the dynamical matrix (4.6). If in (4.6) one replaces $\boldsymbol{q}$ by $-\boldsymbol{q}$, then this corresponds in the definition of the dynamical matrix merely to a renaming of the indices $\boldsymbol{m}$ and $\boldsymbol{n}$. However, the dynamical matrix is not dependent on these indices. Taking these facts together we see that it suffices to represent $\omega(\boldsymbol{q})$ in the region $0 \le q \le G/2$. The point $q = G/2$ lies precisely on the edge of the Brillouin zone introduced in Sect. 3.5. Thus the function $\omega(\boldsymbol{q})$ can be fully specified by giving its values in one octant of the Brillouin zone.

For the example of the diatomic linear chain, Fig. 4.3 shows the two branches of the dispersion relation for a mass ratio of $M_1/M_2 = 5$. The branch that goes to zero at small q is known as the *acoustic* branch. For this branch, at small $q (q \ll \pi/a)$ the angular frequency ω is proportional to the wave vector q. Here the acoustic branch describes the dispersion-free propagation of sound waves.

The branch for which $\omega(q) \neq 0$ at $q = 0$ is called the *optical* branch. Its frequencies at $q = 0$ and $q = \pi/a$ have a simple interpretation. For $q = 0$ the displacements of the atoms in every unit cell are identical. The sublattices of light and heavy atoms are vibrating against one another. In this case the

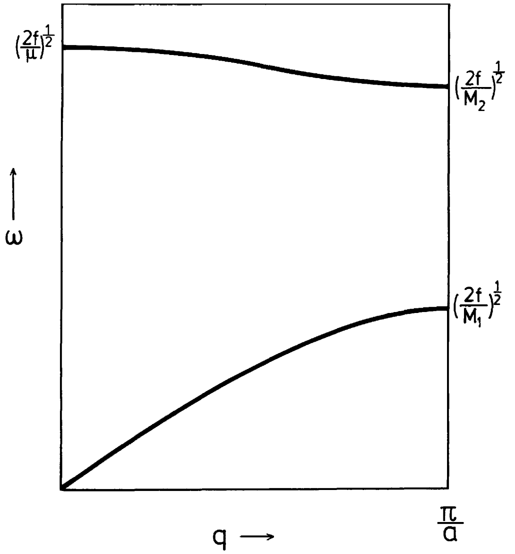


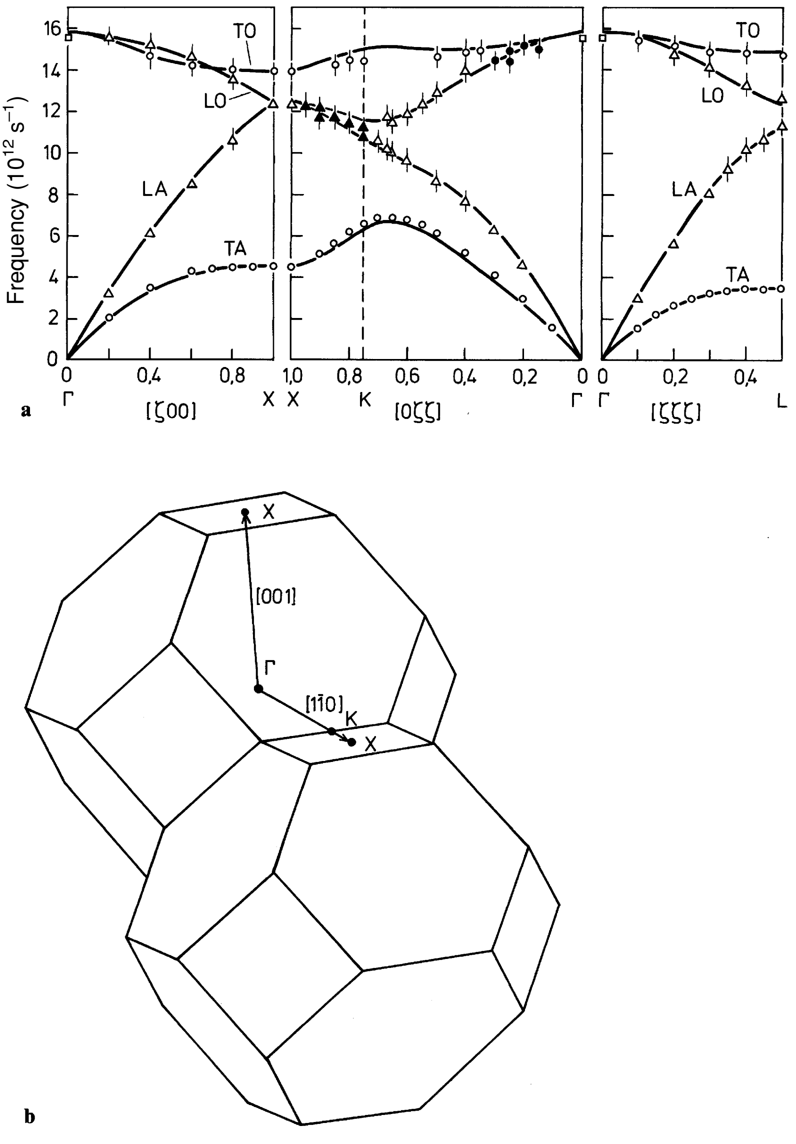
Fig. 4.3. Dispersion curve of a diatomic linear chain with a mass ratio $M_1/M_2 = 5$. With increasing mass ratio, the optical branch becomes progressively flatter

problem can be reduced to a system of two masses with force constant $2f$ and the reduced mass $1/\mu = 1/M_1 + 1/M_2$. At $q = \pi/a$, one or other of the two sublattices is at rest and thus the two frequencies at this wave vector are $(2f/M_2)^{1/2}$ and $(2f/M_1)^{1/2}$.

The diatomic linear chain model is a popular tool for describing vibrations in ionic crystals, in which neighboring sites are occupied by ions of opposite charge. If an optical mode is present at $q \simeq 0$ then the positive ions within the unit cell move in the opposite direction to the negative ones, i.e. an oscillating dipole moment is created. This can couple to an external oscillating electric field (e.g., infrared radiation) which means that such vibrations are "infrared active", i.e. they cause infrared light to be absorbed (Chap. 11).

For the diatomic linear chain we only allowed displacements of the atoms along the direction of the chain. Such waves are called longitudinal waves. For a three-dimensional crystal there are two additional transverse waves. However, the clear separation of the vibrational modes into longitudinal and transverse is only possible in certain symmetry directions of the crystal. For an arbitrary direction the waves have a mixed character. Every crystal has three acoustic branches. For small q values (long wavelengths) these correspond to the sound waves of elasticity theory (4.5). For every additional atom in the unit cell one obtains a further three optical branches. Here the enumeration of the atoms must be referred to the smallest possible unit cell. For the fcc structure, in which many metals crystallize, the conventional unit cell contains four atoms, but the smallest possible cell contains only one atom (Fig. 2.8). Such crystals therefore possess only acoustic branches. The same is true for the bcc structure.

Although a crystal may be said to have three acoustic branches, this does not necessarily mean that these must everywhere have different frequencies. In cubic structures for example, the two transverse branches are degenerate along the [001] and [111] directions. This also holds for the diamond structure (Fig. 4.4). In the latter case, the smallest possible unit cell contains two atoms and thus, along with the acoustic branches, there are also optical branches.



It should be noted that "optical" is the term used to describe all branches that have a non-zero frequency at $q = 0$. It does not necessarily imply optical activity, as can be demonstrated for the case of the diamond structure. At $q = 0$ in the optical branch the two fcc substructures of the diamond structure vibrate against one another. However, since these two substructures are occupied by identical atoms, this vibration does not give rise to a dipole moment and hence it cannot interact with light. The optical modes are 3-fold degenerate at $q = 0$. In Sect. 2.4 we saw that such 3-fold degeneracy is only possible for the point groups of cubic structures.

In contrast to the diamond structure, the zinc-blende structure consists of two substructures that are occupied by different atoms. "Optical" vibrations of this structure do lead to an oscillating dipole moment, which in turn gives rise to the absorption of electromagnetic radiation in this frequency range. In Chap. 11 we will see that this also lifts the degeneracy between the longitudinal- and transverse-optical waves.

4.4 Scattering from Time-Varying Structures – Phonon Spectroscopy

The solutions of the equations of motion for the atoms have the form of plane waves. In analogy to the wave-particle dualism of quantum mechanics, one might ask whether these waves can also be interpreted as particles. Any such particle aspect would manifest itself, for example, in the interaction with other particles, i.e., electrons, neutrons, atoms and photons. Thus we shall now extend the scattering theory developed in Chap. 3 to the case of structures that are time varying. The problem will again be treated in a quasi-classical framework. Later on, when we consider electron-phonon scattering (Chap. 9), we shall also meet the quantum-mechanical formalism.

We return to the scattering amplitude A_B derived in (3.6):

$$A_B \propto \mathrm{e}^{-\mathrm{i}\omega_0 t} \int \varrho(\boldsymbol{r}(t))\mathrm{e}^{-\mathrm{i}\boldsymbol{K}\cdot\boldsymbol{r}(t)} d\boldsymbol{r} \,. \tag{4.20}$$

Fig. 4.4. (**a**) Phonon dispersion curves of Si. The circles and triangles are measured points and the solid lines are the result of a model calculation by Dolling and Cowley [4.3]. Instead of the wave vector $\boldsymbol{q}$, one often uses the reduced wave vector $\boldsymbol{\zeta} = \boldsymbol{q}/(2\pi/a)$ as the coordinate for such plots. The relative lengths of the abscissae correspond to the actual separation of the points in the Brillouin zone. The branches of the dispersion curves carry the notation TA (transverse acoustic), LA (longitudinal acoustic), TO (transverse optical) and LO (longitudinal optical). Along the [100] and [111] directions the transverse branches are degenerate. Concerning the degeneracy of LO and TO at Γ, see also Sect. 11.4. (**b**) A sketch of two neighboring Brillouin zones showing that by moving along [110] from Γ to K one can arrive at X by continuing along the adjoining Brillouin zone boundary. Thus the point X can be described either by the wave vector $\boldsymbol{q} = 2\pi/a$ [001] or by $\boldsymbol{q} = 2\pi/a$ [110]. By studying the fcc lattice (Figs. 2.8, 12), one can convince oneself that these two $\boldsymbol{q}$-vectors describe the same atomic motion

To simplify the mathematics we consider a primitive structure and assume the atoms to be point-like scattering centers situated at the time-dependent positions $\boldsymbol{r}_{\boldsymbol{n}}(t)$. Thus we write $\varrho(\boldsymbol{r},t) \propto \sum_{\boldsymbol{n}} \delta(\boldsymbol{r}-\boldsymbol{r}_{\boldsymbol{n}}(t))$

$$A_B \propto \mathrm{e}^{-\mathrm{i}\omega_0 t} \sum_{\boldsymbol{n}} \mathrm{e}^{-\mathrm{i}\boldsymbol{K}\cdot\boldsymbol{r}_{\boldsymbol{n}}(t)} \; . \tag{4.21}$$

We separate each of the time-dependent vectors $\boldsymbol{r}_n(\mathrm{t})$ into a lattice vector $\boldsymbol{r}_{\boldsymbol{n}}$ and a displacement from the lattice site $\boldsymbol{u}_n(\mathrm{t})$

$$\boldsymbol{r}_{\boldsymbol{n}}(t) = \boldsymbol{r}_{\boldsymbol{n}} + \boldsymbol{u}_{\boldsymbol{n}}(t) \; . \tag{4.22}$$

With this one obtains

$$A \propto \sum_{\boldsymbol{n}} \mathrm{e}^{-\mathrm{i}\boldsymbol{K}\cdot\boldsymbol{r}_{\boldsymbol{n}}} \, \mathrm{e}^{-\mathrm{i}\boldsymbol{K}\cdot\boldsymbol{u}_{\boldsymbol{n}}(t)} \, \mathrm{e}^{-\mathrm{i}\omega_0 t} \; . \tag{4.23}$$

For small displacements $\boldsymbol{u}_{\boldsymbol{n}}(t)$ we can make the expansion

$$A \propto \sum_{\boldsymbol{n}} \mathrm{e}^{-\mathrm{i}\boldsymbol{K}\cdot\boldsymbol{r}_{\boldsymbol{n}}} \, [1 - \mathrm{i}\,\boldsymbol{K}\cdot\boldsymbol{u}_{\boldsymbol{n}}(t)\ldots]\mathrm{e}^{-\mathrm{i}\omega_0 t} \; . \tag{4.24}$$

With the most general form of the expansion in terms of plane waves

$$\boldsymbol{u}_{\boldsymbol{n}}(t) = \boldsymbol{u}\frac{1}{\sqrt{M}}\mathrm{e}^{\pm\mathrm{i}[\boldsymbol{q}\cdot\boldsymbol{r}_{\boldsymbol{n}} - \omega(\boldsymbol{q})t]} \tag{4.25}$$

we obtain, besides the familiar elastic scattering, the terms

$$A_{\mathrm{inel}} \propto \sum_{\boldsymbol{n}} \mathrm{e}^{-\mathrm{i}(\boldsymbol{K}\mp\boldsymbol{q})\cdot\boldsymbol{r}_{\boldsymbol{n}}} \, \mathrm{i}\boldsymbol{K}\cdot\boldsymbol{u}\frac{1}{\sqrt{M}}\mathrm{e}^{-\mathrm{i}[\omega_0 \pm \omega(\boldsymbol{q})]t} \; . \tag{4.26}$$

Thus there are scattered waves for which the frequency ω differs from that of the primary wave by exactly the frequency of the crystal vibration. These scattered waves must obey a further condition relating to the wave vector since the sum over $\boldsymbol{n}$ only yields contributions when $\boldsymbol{K}\mp\boldsymbol{q}$ is equal to a reciprocal lattice vector $\boldsymbol{G}$

$$\begin{aligned} &\omega = \omega_0 \pm \omega(\boldsymbol{q}) \; , \\ &\boldsymbol{k} - \boldsymbol{k}_0 \mp \boldsymbol{q} = \boldsymbol{G} \; . \end{aligned} \tag{4.27}$$

On multiplying both equations by $\hbar$:

$$\begin{aligned} &\hbar\omega - \hbar\omega_0 \mp \hbar\omega(\boldsymbol{q}) = 0 \; , \\ &\hbar\boldsymbol{k} - \hbar\boldsymbol{k}_0 \mp \hbar\boldsymbol{q} - \hbar\boldsymbol{G} = \boldsymbol{0} \; , \end{aligned} \tag{4.28}$$

one sees that the first of these classical equations can be interpreted quantum mechanically as the conservation of energy. The plus sign corresponds to the excitation of a crystal vibration by the scattered particle; the minus sign applies to processes in which a crystal vibration loses energy to the scattered particle. The latter possibility can of course only occur if the crystal vibration has sufficient initial energy (amplitude of excitation); see (5.8). The second of the conditions in (4.28) can be interpreted as the conservation of quasimomentum, if it is assumed that $\hbar \boldsymbol{q}$ is the quasimomentum of the wave-like crystal vibration. Thus, in the sense of the conservation equations (4.28), one can regard these waves as particles. The term commonly used to describe such "particles" is *phonons*. The quasimomentum of phonons, however, is unlike a normal momentum because it is only defined to within an arbitrary reciprocal lattice vector. Furthermore, it has nothing to do with the momentum of the individual atoms. For these we have $\sum_i m_i v_i \equiv 0$ at all times because of the nature of the solutions of the equations of motion (Problem 4.2). Hence the term "quasimomentum" for the quantity $\hbar \boldsymbol{q}$.

It should be emphasized that the derivation of the conservation equations (4.28) proceeded via a purely classical treatment of the motion of the crystal atoms. Thus the particle model of phonons that emerges here is not a quantum mechanical result. It can, however, be quantum mechanically justified if one begins with the general quantization rules for equations of motion.

The momentum and energy conservation laws that govern the inelastic interaction of light and particle waves with phonons can be used to advantage for the experimental determination of phonon dispersion curves. We first discuss the interaction with light.

The inelastic scattering of light in and around the visible region is known either as Raman scattering, or, when the interaction is with acoustic waves, as Brillouin scattering. The scattering is produced by the polarization of the atoms in the radiation field and the subsequent emission of dipole radiation. In the frequency range of visible light the maximum wave vector transfer is

$$2k_0 = \frac{4\pi}{\lambda} \sim 2 \cdot 10^{-3} \text{Å}^{-1} \ ,$$

i.e., approximately 1/1000 of a reciprocal lattice vector. Thus Raman scattering can only be used to study lattice vibrations near to the center of the Brillouin zone (i.e., around $q = 0$) (Panel III).

This would not be the case for the inelastic scattering of X-rays. With X-rays, as we saw in the discussion of diffraction, one can readily have wave-vector transfers of the order of reciprocal lattice vectors. The photon energy of such X-rays is around 10^4 eV. The natural width of characteristic X-ray lines is about 1 eV, whereas phonon energies lie in the range 1–100 meV. To perform phonon spectroscopy one would therefore have to monochromate the X-rays to within about 1 meV; for this, one could use a crystal monochromator. The energy selection is achieved, as with an optical grating (Panel XII), by making use of the wavelength dependence of the diffraction. If one differentiates the Bragg equation

$$\begin{aligned} \lambda &= 2d \sin\theta \ , \\ \Delta\lambda &= 2\Delta d \sin\theta + 2d\Delta\theta\cos\theta \ , \end{aligned} \tag{4.29}$$

one obtains an expression for the monochromaticity of the beam as a function of the angular aperture $\Delta\theta$ and the deviation Δd of the lattice constant from its mean value (Panel II)

$$\frac{\Delta\lambda}{\lambda} = -\frac{\Delta E}{E} = \frac{\Delta d}{d} + \Delta\theta \operatorname{ctg}\theta\,. \tag{4.30}$$

For X-rays one would require $\Delta\lambda/\lambda \sim 10^{-7}$. The corresponding angular aperture would be so small that only the use of X-rays from synchrotron sources (Panel XI) would provide sufficient intensity. Furthermore, it is very difficult to find crystals that are sufficiently perfect and stress-free to fulfill the condition $\Delta d/d \sim 10^{-7}$ (Panel II). Using synchrotron beams, however, it is possible to obtain an energy resolution of just a few meV.

For neutrons and atoms, however, the prerequisites for phonon spectroscopy are far more realistic. The primary energies needed to give the required wave-vector transfer now lie in the range 0.1–1 eV ($\Delta\lambda/\lambda \sim 10^{-2}$–$10^{-3}$). Such neutrons are readily available in the form of the thermal neutrons produced by reactors (Panel I). Inelastic neutron scattering has been used to determine the phonon dispersion curves of most materials. As an example, Fig. 4.4 shows the dispersion curves for Si.

4.5 Elastic Properties of Crystals

In the limit of long wave length ($q \to 0$) the frequency of phonons in the "acoustic branches" is proportional to the wave vector q. For these acoustical phonons of long wave length, the sound waves, the displacement vectors in neighboring unit cells are nearly equal. The state of deformation of the crystal can be therefore described in the framework of a continuum theory. We consider the transition from atom dynamics to the continuum theory of elasticity for a particular example, namely a simple cubic crystal with nearest-neighbor bonds in the form of springs (Fig. 4.5). The model is an unrealistic representation of the elastic properties of a real solid since it has no stability with regard to shearing. However, it suffices for a general consideration of longitudinal waves along a cubic axis. The

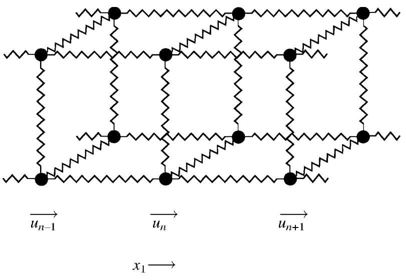


Fig. 4.5. Generalization of the linear chain spring model into three dimensions to represent a cubic primitive crystal. While the model with springs to nearest-neighbors is lacking stability against shear it suffices for a simple ansatz for longitudinal sound waves along a cubic axis

coordinate along the cubic axis and the components of the displacement vectors in the nth elementary cell in the direction of the axis are denoted as x_1 and u_{n1}, respectively. For a longitudinal wave along a cubic axis all displacement vectors perpendicular to this axis are equal. Furthermore, only the springs connecting atoms along the axis of propagation are strained. The equation of motion therefore becomes one-dimensional as for the linear chain (4.11).

$$M\ddot{u}_{n1} = f(u_{(n+1),1} - u_{n1}) - f(u_{n1} - u_{(n-1),1})\,. \tag{4.31}$$

If the displacements vary little from cell to cell the differences can be replaced by the differential quotients.

$$\begin{aligned}(u_{(n+1),1} - u_{n1}) - (u_{n1} - u_{(n-1),1}) &= a\frac{\partial u_1}{\partial x_1}\bigg|_{x=(n+1/2)a} - a\frac{\partial u_1}{\partial x_1}\bigg|_{x=(n-1/2)a}\\ &= a^2\frac{\partial^2 u_1}{\partial x_1^2}\bigg|_{x=na}\,.\end{aligned} \tag{4.32}$$

The derivative

$$\varepsilon_{11} = \frac{\partial u_1}{\partial x_1}\,, \tag{4.33}$$

which is called the *strain,* is already a continuum quantity. The strain describes the change in the displacements of the atoms per length, hence a stretch and a compression of the material for $\varepsilon_{11} > 0$ and $\varepsilon_{11} < 0$, respectively. From (4.32) we see that the restoring elastic force in the x_1-direction is proportional to the derivative of the local strain ε_{11} with respect to the coordinate x_1. If, furthermore, the masses of atoms are replaced by the mass density $\varrho = M/a^3$, then the continuum equation of motion for a longitudinal sound wave is obtained.

$$\varrho\ddot{u}_1 = c_{11}\frac{\partial^2 u_1}{\partial x_1^2} \quad \text{with} \quad c_{11} = \frac{f}{a}\,. \tag{4.34}$$

The quantity c_{11} is an elastic modulus that describes the force per unit area in the x_1-direction in response to a deformation along the same axis. The sound velocity of the longitudinal wave is

$$c_L = \sqrt{\frac{c_{11}}{\varrho}}\,. \tag{4.35}$$

The continuum equation of motion (4.34) for the longitudinal sound wave along a cubic axis is valid for all cubic crystals. Only the relation between the elastic modulus and the interatomic potential is specific for the structure and the interatomic force field. Thus, the relation is different for fcc, bcc, or the diamond structure.

Up to now we were interested in the forces along the cubic axis that occurred in response to a deformation along the same axis. Now general deformations and forces are considered. We begin with a generalization of (4.33), the definition of a deformation

$$\varepsilon_{ij} = \frac{\partial u_i}{\partial x_j} \,. \tag{4.36}$$

The quantity ε_{ij} is a second rank-tensor. As a matter of convenience the components of the tensor are expressed in terms of particular cartesians that are chosen to agree as much as possible with the crystallographic axes. The diagonal elements of the tensor ε_{ii} describe infinitesimal distortions associated with a change in volume (Fig. 4.6 a). The magnitude of the (infinitesimal) change in the volume is given by the trace of the deformation tensor

$$\frac{\Delta V}{V} = \sum_i \varepsilon_{ii} \,. \tag{4.37}$$

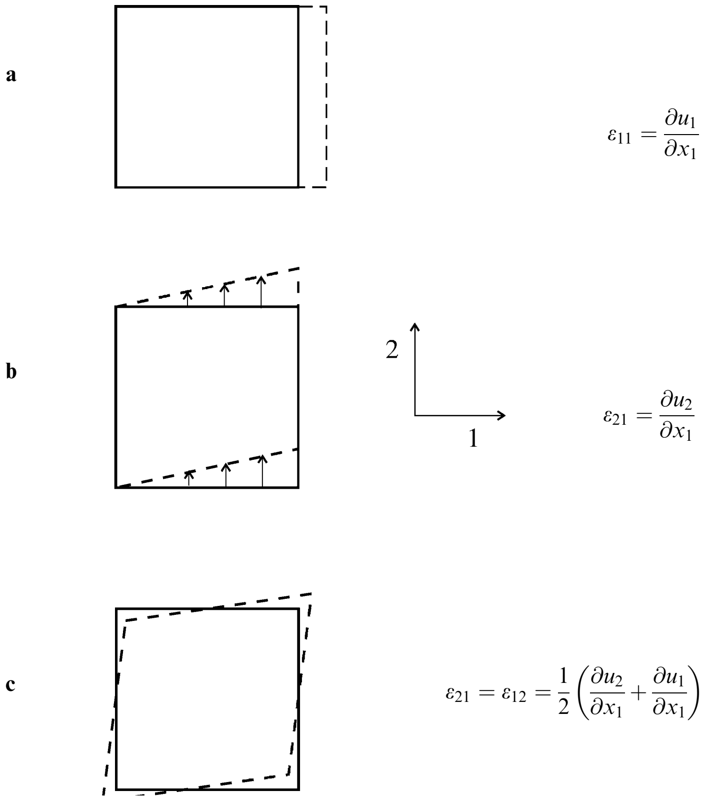


Fig. 4.6. Illustrations to elucidate the terminology in the theory of elasticity. (**a**) Strain along the x_1-axis; (**b**) shear along the x_2-axis, without separation of the rotational part of ε_{21}; (**c**) the same shear after splitting off the rotational component by symmetrizing the strain tensor

The nondiagonal elements ε_{ij} describe the deformation of a volume element in the i-direction as one moves along the j-direction and hence correspond to a shear distortion (Fig. 4.6 b). It is useful to split ε_{ij} into a symmetric and an antisymmetric part with respect to an exchange of i and j.

$$\varepsilon_{ij} = \frac{\partial u_i}{\partial x_j} \equiv \frac{1}{2}\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right) + \frac{1}{2}\left(\frac{\partial u_i}{\partial x_j} - \frac{\partial u_j}{\partial x_i}\right) . \tag{4.38}$$

The antisymmetric part $((\partial u_i/\partial x_j) - (\partial u_j/\partial x_i))$ describes a rotation whereas the deformation of the material is given by the symmetric tensor (Fig. 4.6 c)

$$\varepsilon_{ij} = \frac{1}{2}\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right) . \tag{4.39}$$

A solid resists deformations, hence deformations generate forces. For a homogeneous material the forces in response to a strain or shear are proportional to the area upon which the deformation is acting. One therefore relates all forces to the areas upon which they act. For a definition of these area-related forces, the "stresses", one considers a section through the crystal perpendicular to the x_l-axis and removes, in thought, the material on the right hand side of the intersection. The forces per area in the direction k that are necessary to keep the crystal in balance without the removed material are the components of the stress tensor τ_{kl} (Fig. 4.7). The stress tensor is symmetric just as the strain tensor: the antisymmetric part of the stress tensor represents a torque, and in equilibrium all torques must vanish inside a solid.

To first order the relation between stress and strain is linear (Hooks law). In its most general form Hooks law reads

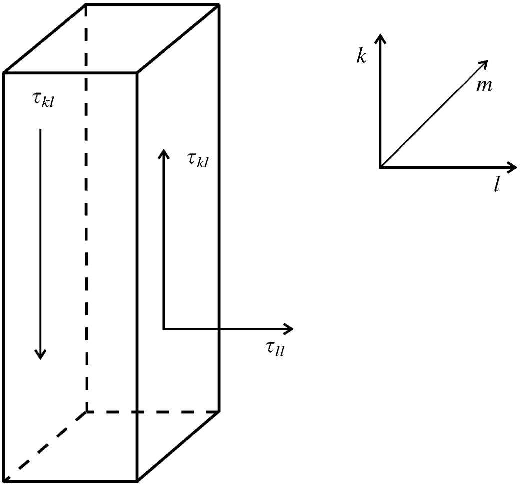


Fig. 4.7. Definition of the shear stress τ_{kl} and the normal stress τ_{ll}

$$\tau_{kl} = \sum_{ij} c_{klij}\varepsilon_{ij} \tag{4.40}$$

with the components of the elastic tensor (modules) c_{klij}. Because of the symmetry of the stress and strain tensors τ_{kl} and ε_{ij} one has the relations

$$c_{klij} = c_{lkij} = c_{klji} \; . \tag{4.41}$$

The number of independent components of the elastic tensor is further reduced by the requirement that the elastic energy be a unique function of the state of strain [4.2]. The energy density u is

$$u = \sum_{kl} \int \tau_{kl} d\varepsilon_{kl} = \tfrac{1}{2} \sum_{ijkl} c_{klij}\varepsilon_{ij}\varepsilon_{kl} \; . \tag{4.42}$$

This equation yields the same result independent of the chosen indices for the axes if

$$c_{klij} = c_{ijkl} \; . \tag{4.43}$$

The relations (4.41) and (4.43) permit a short-hand notation introduced by Voigt. In this notation a number between 1 and 6 is attributed to each pair of indices i and j. The assignment follows the scheme

$$\begin{aligned} 11 &\to 1 \quad 23 \to 4 \\ 22 &\to 2 \quad 13 \to 5 \\ 33 &\to 3 \quad 12 \to 6 \; . \end{aligned} \tag{4.44}$$

Components of the stress and strain tensor can also be denoted using Voigt's notation. In order to ensure that all non diagonal elements of the strain and stress tensor in the energy density (4.42) are properly accounted for (i.e. ε_{ij} and ε_{ji}) a complete transition to Voigt's notation requires the introduction of redefined elastic modules. For our purpose here it is easier to use Voigt's notation only as an abbreviation for the indices in the elastic modules and stay with the standard tensor notation and summation otherwise. In the short-hand notation the elastic tensor becomes a 6×6 symmetric tensor with 21 independent components, at most. The number of independent components is further reduced by the crystal symmetry. For crystals with cubic symmetry the elastic tensor has only three independent components

$$\begin{pmatrix} c_{11} & c_{12} & c_{12} & 0 & 0 & 0 \\ c_{12} & c_{11} & c_{12} & 0 & 0 & 0 \\ c_{12} & c_{12} & c_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & c_{44} \end{pmatrix} \; . \tag{4.45}$$

It is easy to see that the elastic tensor must have this form, even without a formal proof. For example, the cubic axes are equivalent. Therefore, the diagonal components for normal and shear distortions must be equal ($c_{11} = c_{22} = c_{33}$ and $c_{44} = c_{55} = c_{66}$). A shear strain along one cubic axis cannot give rise to forces that would cause a shear along another cubic axis ($c_{45} = 0$, etc.). Furthermore, a shear cannot cause a normal stress ($c_{14} = 0$, etc.), and finally the forces perpendicular to a strain along one cubic axis must be isotropic ($c_{12} = c_{13}$, etc.).

For a hexagonal crystal the elastic tensor has the components

$$\begin{pmatrix} c_{11} & c_{12} & c_{13} & 0 & 0 & 0 \\ c_{12} & c_{11} & c_{13} & 0 & 0 & 0 \\ c_{13} & c_{13} & c_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & c_{66} \end{pmatrix} . \tag{4.46}$$

A hexagonal crystal is elastically isotropic in its basal plane. The tensor component that describes the stress-strain relation for a shear distortion in the basal plane, c_{66}, is therefore related to the tensor components c_{11} and c_{12} by the "isotropy condition" (see also 4.65)

$$2c_{66} = c_{11} - c_{12} . \tag{4.47}$$

With the help of the elastic tensor we can now generalize the wave equation (4.34). As noted before, we keep the standard double indices for the stress and strain tensors. The force that acts upon an infinitesimal cubicle of the volume $dV = dx_1dx_2dx_3$ in a direction k can be expressed in terms of the forces acting upon the faces of the cubicle

$$\begin{aligned} dF_k &= (\tau_{k1}(x_1 + dx_1) - \tau_{k1}(x_1))dx_2dx_3 \\ &\quad + (\tau_{k2}(x_2 + dx_2) - \tau_{k2}(x_2))dx_1dx_3 \\ &\quad + (\tau_{k3}(x_3 + dx_3) - \tau_{k3}(x_3))dx_1dx_2 \\ &= dV \sum_l \frac{\partial \tau_{kl}}{\partial x_l} \\ &= dV \sum_{ijl} c_{klij} \frac{1}{2} \left(\frac{\partial^2 u_i}{\partial x_l \partial x_j} + \frac{\partial^2 u_j}{\partial x_l \partial x_i} \right) \\ &\equiv dV \sum_{ijl} c_{klij} \frac{\partial^2 u_i}{\partial x_l \partial x_j} . \end{aligned} \tag{4.48}$$

The sum of the elastic forces and the force of inertia $\varrho dV \ddot{u}_k$ must be zero. Hence, the generalized equation for the propagation of elastic waves in a crystalline solid of arbitrary symmetry is:

$$\varrho \ddot{u}_k = \sum_{ijl} c_{klij} \frac{\partial^2 u_i}{\partial x_l \partial x_j} \ . \tag{4.49}$$

In general (4.49) represents three coupled equations with three independent solutions. The equations decouple for particular high-symmetry orientations where entries in the elastic tensor vanish. A simple example are the sound waves along the axis of a cubic crystal. The solutions of (4.49) are a longitudinal and two degenerate transverse sound waves. If one chooses the x_1-axis as the direction of propagation and considers the motion along the x_2-axis the only non-vanishing derivative is

$$\frac{\partial^2 u_2}{\partial x_1 \partial x_1} \neq 0 \ , \tag{4.50}$$

and one obtains the equation of motion for the transverse sound wave:

$$\varrho \ddot{u}_2 = c_{2121} \frac{\partial^2 u_2}{\partial x_1^2} = c_{44} \frac{\partial^2 u_2}{\partial x_1^2} \ , \tag{4.51}$$

with the sound velocity

$$c_\mathrm{T} = \sqrt{\frac{c_{44}}{\varrho}} \ . \tag{4.52}$$

In many cases it is useful to work with the inverse of the elastic tensor c_{ijkl}. The inverse tensor s_{ijkl} is defined by the equation

$$\varepsilon_{ij} = \sum_{kl} s_{ijkl} \tau_{kl} \ . \tag{4.53}$$

The relations between the tensor components of $\boldsymbol{c}$ and $\boldsymbol{s}$ can be calculated by a formal tensor inversion, but also by describing certain states of strain. Consider, e.g., an isotropic deformation of a cubic crystal

$$\varepsilon_{ij} = \varepsilon \delta_{ij} \ . \tag{4.54}$$

Because of the cubic symmetry the stresses must likewise be isotropic

$$\tau_{ij} = \tau \delta_{ij} \ . \tag{4.55}$$

In that case, the elastic equations (4.43 and 4.53) reduce to

$$\begin{aligned} \tau &= (c_{11} + 2c_{12})\varepsilon \ , \\ \varepsilon &= (s_{11} + 2s_{12})\tau \ , \end{aligned} \tag{4.56}$$

and one obtains the relation

$$(c_{11} + 2c_{12})(s_{11} + 2s_{12}) = 1 \ . \tag{4.57}$$

We learn from (4.57), that a measurement of the volume change of a cubic crystal under hydrostatic pressure yields the combination of the elastic constants $c_{11} + 2c_{12}$ and $s_{11} + 2s_{12}$, respectively.

A second relation between the elastic modules $\boldsymbol{c}$ and the elastic constants $\boldsymbol{s}$

$$(c_{11} - c_{12})(s_{11} - s_{12}) = 1 \tag{4.58}$$

is obtained by an analogous consideration of the strain state $\varepsilon_{11} = -\varepsilon_{22}$, $\varepsilon_{33} = 0$, with $\varepsilon_{ij} = 0$ for $i \neq j$. By combining (4.57) and (4.58) one obtains

$$\begin{aligned} s_{11} &= \frac{1}{3}\left(\frac{1}{c_{11} + 2c_{12}} + \frac{2}{c_{11} - c_{12}}\right) , \\ s_{12} &= \frac{1}{3}\left(\frac{1}{c_{11} + 2c_{12}} - \frac{1}{c_{11} - c_{12}}\right) . \end{aligned} \tag{4.59}$$

Because of the diagonal form of the elastic tensor for shear stresses and strains (4.45) one has furthermore

$$c_{44} = 1/s_{44} \; . \tag{4.60}$$

The relations (4.58) and (4.60) hold also for hexagonal and the most important tetragonal crystals. Equation (4.57) is replaced by the set of equations

$$\begin{aligned} &(c_{11} + c_{12}) = s_{33} s^{-1} \; , \\ &c_{13} = -s_{13} s^{-1} \; , \\ &c_{33} = (s_{11} + s_{12}) s^{-1} \; , \\ &\text{with } s = s_{33}(s_{11} + s_{12}) - 2s_{13}^2 \; . \end{aligned} \tag{4.61}$$

Furthermore, one has $c_{66} = s_{66}^{-1}$.

Despite its high symmetry, a cubic crystal is not elastically isotropic. The stress arising from a deformation along a cubic axis differs from the stress arising from a deformation along the diagonal. In order to be elastically isotropic the elastic constants of cubic crystals must fulfill a particular condition. In order to derive this isotropy condition we consider a cubic crystal that is strained along an arbitrarily oriented x-axis by the amount ε_{xx} and compressed along the perpendicular y-axis by $\varepsilon_{yy} = -\varepsilon_{xx}$. If the cubic axes x_1 and x_2 are parallel to x- and y-axes, one obtains for the stress τ_{xx}

$$\tau_{xx} = (c_{11} - c_{12})\varepsilon_{xx} \; . \tag{4.62}$$

If the cubic axes are rotated with respect to the x- and y-axis by 45° then the deformation corresponds to a shear deformation in the cubic axes (Fig. 4.8). By writing the components of the strain tensor in the cubic axes and in the x- and y-axis in terms of the displacement vector s_2 (Fig. 4.8), it is easy to see that $\varepsilon_{23} = \varepsilon_{xx}$. We thus obtain for the stress

$$\tau_{23} = c_{44}\varepsilon_{23} = c_{44}\varepsilon_{xx} \; . \tag{4.63}$$

We now express τ_{23} by τ_{xx}. On a cube with an edge length a the stress τ_{xx} exerts the force

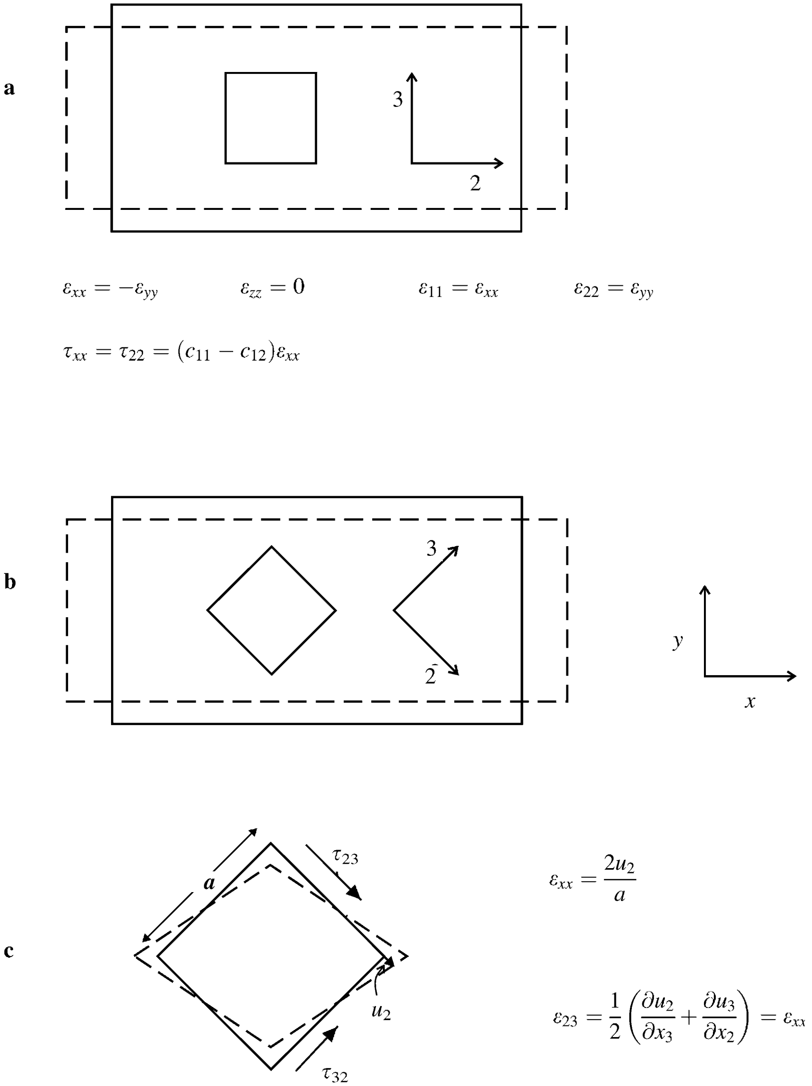


Fig. 4.8. For the derivation of the condition for elastic isotropy one considers a volume-conserving deformation of a material under the assumption that (**a**) the deformation is along the cubic axes and (**b**) that the strain directions form an angle of 45° with the cubic axes. The deformation (**b**) corresponds to a shear in the cubic axes. For an isotropic material the resulting stresses must be identical in both cases. This condition yields the isotropy relation between the elastic constants (4.66)

$$f_x = \tau_{xx} a^2/\sqrt{2} \,. \tag{4.64}$$

Projected into the direction x_2 one has the force

$$f_2 = \tau_{23} a^2 = f_x/\sqrt{2} = \tau_{xx} a^2/2 \,. \tag{4.65}$$

Table. 4.1. Elastic constants for several cubic crystals at 20 °C (after [4.6]). The moduli c_{ij} are in $10^{10}\,\mathrm{N/m^2}$ and the constants (compliances) s_{ij} in $10^{-12}\,\mathrm{m^2/N}$. The numbers refer to the cubic axes. For a transformation into arbitrarily rotated axes see [4.4, 4.5]. The reliability and accuracy of the data differs for the various materials because of the different quality of available crystals. The temperature dependence of the elastic constant is particularly large for potassium and sodium. These materials become significantly stiffer at low temperatures. The condition for elastic isotropy, $2c_{44}/(c_{11}-c_{12})=1$, is fulfilled only in exceptional cases. Many metals are surprisingly anisotropic (see last column)

Material	s_{11}	s_{44}	s_{12}	c_{11}	c_{44}	c_{12}	$\frac{2c_{44}}{c_{11}-c_{12}}$
K	1225	530	–560	0.37	0.19	0.31	6.3
Na	590	240	–270	0.74	0.42	0.62	7.0
Ta	6.86	12.1	–2.58	26.7	8.25	16.1	1.56
Cr	3.05	9.9	–0.495	35.0	10.0	6.78	0.71
Mo	2.8	9.1	–0.78	45.5	11.0	17.6	0.79
W	2.53	6.55	–0.726	50.1	15.1	20.5	1.0
Fe	7.7	8.9	–2.8	23.7	11.6	14.1	2.4
Ir	2.28	3.91	–0.67	58.0	25.6	24.2	1.5
Ni	7.7	9.0	–3.0	24.4	11.2	15.4	2.5
Pd	13.6	13.9	–5.95	22.7	7.17	17.6	2.8
Pt	7.34	13.1	–3.08	34.6	7.64	25	1.44
Cu	15.0	13.3	–6.3	16.8	7.54	12.1	3.2
Ag	22.9	21.7	–9.8	12.4	4.6	9.35	3.0
Au	23.3	23.8	–10.7	18.6	4.2	16.3	3.7
Al	15.7	35.9	–5.8	11.2	2.8	6.6	1.2
C	1.48	1.74	–0.517	107.6	57.6	12.5	1.21
Si	7.68	12.56	2.14	16.57	7.96	6.39	1.56
Ge	9.75	14.9	–2.66	12.9	6.71	4.83	1.66
GaAs	12.6	18.6	–4.23	11.9	5.4	6.0	1.83
LiF	11.35	15.9	–3.1	11.1	6.3	4.2	1.82
NaCl	22.9	79.4	–4.65	4.87	1.26	1.24	0.69

With (4.63) and (4.65) and by comparison to (4.62) one obtains the condition for elastic isotropic behavior

$$2c_{44} = c_{11} - c_{12} \; . \tag{4.66}$$

Because of this condition an elastic isotropic solid has only two independent constants that are denoted as

$$\lambda = c_{12} \quad \mu = c_{44} \; . \tag{4.67}$$

Hooks law (4.40) then becomes

$$\tau_{ik} = \lambda\delta_{ik}\sum_i \varepsilon_{ii} + 2\mu\varepsilon_{ik} \; . \tag{4.68}$$

In mechanical engineering Young's modulus Y (also denoted by E) and the Poisson number ν are commonly used. Young's modulus describes the change in length of a rod in response to a pull and ν describes the relative contraction perpendicular to the direction of pull. The constants Y, ν, λ μ, and the elastic constants s_{ij} in the cubic system are related by:

$$\nu = \frac{\lambda}{2(\lambda+\mu)} = -\frac{s_{12}}{s_{11}} \quad Y = \frac{\mu(2\mu+3\lambda)}{\mu+\lambda} = \frac{1}{s_{11}} \ . \tag{4.69}$$

Note that Y is merely the inverse of s_{11} and not a component of the inverse tensor of modules $\boldsymbol{c}$, although it has the dimension of a modulus!

Problems

4.1 Localized vibrations in a crystal can be represented by a superposition of phonon modes with different wave vectors. Show that the center of gravity of such a wave packet moves with the group velocity $v_g = d\omega/dq$.

4.2 Write down the dynamic equation for a one-dimensional linear chain of N (large number) atoms (atomic distance a, restoring force f, atomic mass m) and solve this with an ansatz $u_n(t) = u(q)\exp[\mathrm{i}(qna-\omega t)]$.

a) Compare the obtained dispersion $\omega(q)$ with that of the diatomic linear chain (4.15).

b) Show that the total momentum $\sum_{n=1}^{N} m\dot{u}_n(t)$ of a phonon vanishes.

c) Show that for long wavelengths ($q \ll a^{-1}$) the dynamic equation for the chain transforms into a wave equation for elastic waves when the displacements $u_n(t) = u(x = na, t)$, $u_{n+1}(t)$ and $u_{n-1}(t)$ are evaluated in a Taylor series.

4.3 Calculate the eigenfrequency of a mass defect $M \neq m$ in a linear chain at the position $n = 0$ by invoking the ansatz $u_n = u_0\exp(-\kappa|n|-\mathrm{i}\omega t)$ for the displacements. For which range of M do localized vibrations exist?

4.4 Calculate the dispersion relation for longitudinal and transverse phonons along the [100] direction of a fcc crystal whose atoms are joined to their nearest neighbors by springs. Using symmetry arguments, first identify any possible degeneracy. In which other high-symmetry direction does a similar consideration apply?

Then try to describe the phonons such that the equation of motion for a linear chain becomes applicable. For this it is important to be aware of the effect of the position of the phase planes on the displacements of the atoms.

Draw the displacements of the atoms for various phonons at the edge of the Brillouin zone.

4.5 Calculate the sound velocity of longitudinal and transverse acoustic modes along the [100] direction of a fcc crystal using the model of problem 4.4. According to crystal elasticity theory the sound velocities are $c_{\text{long}} = (c_{11}/\varrho)^{1/2}$ and $c_{\text{trans}} = (c_{44}/\varrho)^{1/2}$, where ϱ is the density. Calculate the elastic constant c_{11} and the shear elastic constant c_{44} in terms of the nearest neighbor force constant. Make the force constant such that the maximum vibrational frequency corresponds to 8.85 THz (representative of nickel) and calculate the numerical values of the sound velocities. The experimental values are 5300 m/s and 3800 m/s for the longitudinal and transverse waves, respectively.

4.6 Calculate the frequency of the surface phonon with odd parity (with respect to the mirror plane spanned by the wave vector and the surface normal) at the zone boundary of a (100) surface of an fcc crystal in the [110] direction using the nearest neighbor central force model. What makes this calculation so easy? Can you find another strictly first-layer mode on the same surface?

4.7 Derive the wave vector conservation for inelastic phonon scattering from a 2D periodic layer of atoms. Do the same problem for inelastic scattering from a surface when the incoming wave is damped inside the solid according to $\exp(-z/\lambda)$, with λ the effective mean free path. Assume a primitive lattice for simplicity. Develop an Ewald construction for the wave vector conservation law when the lattice has 2D periodicity.

4.8 Carry the expansion (4.24) one step further and calculate the time average of the scattered amplitude. Rewrite the expansion

$$1 - \tfrac{1}{2}\left\langle(\boldsymbol{K}\cdot\boldsymbol{u}_n)^2\right\rangle_t \approx \mathrm{e}^{-\frac{1}{2}\left\langle(\boldsymbol{K}\cdot\boldsymbol{u}_n)^2\right\rangle_t} \,.$$

By equating the time average with the ensemble average, calculate the scattered intensity for a primitive lattice.

In the prefactor $\exp(-\left\langle(\boldsymbol{K}\cdot\boldsymbol{u}_n)^2\right\rangle_t$ the quantity $W = \frac{1}{2}\left\langle(\boldsymbol{K}\cdot\boldsymbol{u}_n)^2\right\rangle$ is known as the Debye-Waller factor. For a harmonic lattice the result is correct even for arbitrarily large values of $\left\langle(\boldsymbol{K}\cdot\boldsymbol{u}_n)^2\right\rangle$. The proof, however, is not straightforward. Calculate the temperature dependence of the Debye-Waller factor assuming that all atoms vibrate as independent oscillators of a frequency $\hbar\omega$ by using (5.2 and 5.15). Carry out the same calculation based on the Debye model.

4.9 Calculate the elastic constants c_{11}, c_{12} and c_{44} of a face-centered cubic crystal under the assumption of spring forces to the nearest-neighbors. Show that the model crystal is not elastically isotropic! Show that $c_{12} = c_{44}$! This is the Cauchy-relation for cubic crystals. Cauchy relations among the elastic constants hold if the interatomic force field involves only central forces (forces acting between pairs of atoms along the bond direction). In reality, non-central forces such as angle bending valence forces and many-body forces cause deviations from the Cauchy relation. For which materials is the Cauchy-relation approximately fulfilled (see Table 4.1)?

4.10 Calculate the elastic energy per area in a thin epitaxial, pseudomorphic Cu film that is deposited on the (100) surface of Ni! Hint: the strain in the film ε_m is the misfit between the lattice constants, $\varepsilon_m = (a_{\mathrm{Ni}} - a_{\mathrm{Cu}})/a_{\mathrm{Ni}}$. The elastic energy density is $u = t\sum_{ij}\int_0^{\varepsilon_m}\tau_{ij}d\varepsilon_{ij}$, with t the film thickness. Why is there a limit to the thickness of epitaxial, pseudomorphic film growth and what happens, once a critical film thickness is reached?

4.11 Electric analog to the phonon-modes of the monatomic linear chain:

a) The equivalent circuit of a loss-free double line is a series of inductances L_n and capacitances C_n connecting the lines. Show that current and voltage on the double line propagate as plane waves that possess the same dispersion $\omega(k)$ as phonons of the linear chain (4.15) with $M_1 = M_2$.
   Hint: Use Kirchhoff's rules to calculate the current difference I_n–I_{n-1} as function of the voltage difference U_n–U_{n-1} for an element of length a of the double-line consisting of the inductance L_n in series and the parallel capacitance C_n.
b) Consider now a double-line with a continuously distributed inductance L' per length and a continuously distributed capacitance C' per length. Set up the differential equation for the relation between current and voltage and show that the dispersion $\omega(k)$ of the wave-like solution is $\omega \propto k$ as in the continuum limit for phonons in a linear chain.

Panel III
Raman Spectroscopy

Since the development of the laser, Raman Spectroscopy [III.1] has become an important method for investigating elementary excitations in solids, for example, phonons and plasmons. In this type of spectroscopy one studies the inelastic scattering of light by the elementary excitations of interest. This inelastic scattering was already mentioned in Sect. 4.5 in connection with scattering from phonons. As for all scattering from time-varying structures (e.g. vibrations of atoms in a crystal), energy must be conserved and, to within a reciprocal lattice vector $\boldsymbol{G}$, wave vector too, i.e. we have

$$\hbar\omega_0 - \hbar\omega \pm \hbar\omega(\boldsymbol{q}) = 0 \ , \tag{III.1}$$

$$\hbar\boldsymbol{k}_0 - \hbar\boldsymbol{k} \pm \hbar\boldsymbol{q} + \hbar\boldsymbol{G} = \boldsymbol{0} \ , \tag{III.2}$$

where $\omega_0, \boldsymbol{k}_0$ and $\omega, \boldsymbol{k}$ characterize the incident and scattered light waves respectively; $\omega(\boldsymbol{q})$ and $\boldsymbol{q}$ are the angular frequency and the wave vector of the elementary excitation, e.g. phonon. For light in the visible region of the spectrum, $|\boldsymbol{k}_0|$ and $|\boldsymbol{k}|$ are of the order of $1/1000$ of a reciprocal lattice vector (Sect. 4.5), which means that only excitations in the center of the Brillouin zone ($|\boldsymbol{q}| \approx 0$) can take part in Raman scattering.

The interaction of visible light with the solid occurs via the polarizability of the valence electrons. The electric field $\mathscr{E}_0$ of the incident light wave induces, via the susceptibility tensor $\underset{\sim}{\boldsymbol{\chi}}$ a polarization $\boldsymbol{P}$, i.e.

$$\boldsymbol{P} = \varepsilon_0 \underset{\sim}{\boldsymbol{\chi}} \boldsymbol{\mathscr{E}}_0 \quad \text{or} \quad P_i = \varepsilon_0 \sum_j \chi_{ij} \mathscr{E}_{j0} \ . \tag{III.3}$$

The periodic modulation of $\boldsymbol{P}$ leads, in turn, to the emission of a wave – the scattered wave. In a classical approximation, the scattered wave can be regarded as dipole radiation from the oscillating dipole $\boldsymbol{P}$. From the laws of electrodynamics one obtains the energy flux density in direction $\hat{\boldsymbol{s}}$, i.e. the Poynting vector $\boldsymbol{S}$, at distance r from the dipole as

$$\boldsymbol{S}(t) = \frac{\omega^4 P^2 \sin^2 \vartheta}{16\pi^2 \varepsilon_0 r^2 c^3} \, \hat{\boldsymbol{s}} \ . \tag{III.4}$$

Here ϑ is the angle between the direction of observation $\hat{\boldsymbol{s}}$ and the direction of the vibration of $\boldsymbol{P}$. The electronic susceptibility $\underset{\sim}{\boldsymbol{\chi}}$ in (III.3) is now a function of the nuclear coordinates and thus of the displacements associated with the vibration $[\omega(\boldsymbol{q}), \boldsymbol{q}]$. Similarly, $\underset{\sim}{\boldsymbol{\chi}}$ can also be a function of some other collective excitations $X[\omega(\boldsymbol{q}), \boldsymbol{q}]$, for example, the density variations associated with a longitudinal electron plasma wave (Sect. 11.9), or the travelling-wave-like variations of magnetization in an otherwise perfectly ordered ferromagnet (magnons). These "displacements" $X[\omega(\boldsymbol{q}), \boldsymbol{q}]$ can be regarded as perturbations in a formal expansion in X. It suffices to retain the first two terms:

$$\underset{\sim}{\chi} = \underset{\sim}{\chi}^0 + (\partial \underset{\sim}{\chi} / \partial X) X \, . \tag{III.5}$$

As we only need to consider excitations with $q \simeq 0$, we can simplify matters by writing $X = X_0 \cos[\omega(\boldsymbol{q})\, t]$ and, if the electric field $\mathscr{E}_0$ of the incident wave is described by $\mathscr{E}_0 = \hat{\mathscr{E}}_0 \cos \omega_0 . t$, we obtain from (III.3) the polarization appearing in (III.4) as

$$\begin{aligned} \boldsymbol{P} &= \varepsilon_0 \underset{\sim}{\chi}^0 \hat{\mathscr{E}}_0 \cos \omega_0 t + \varepsilon_0 \frac{\partial \underset{\sim}{\chi}}{\partial X} X_0 \, \hat{\mathscr{E}}_0 \cos[\omega(\boldsymbol{q}) t] \cos \omega_0 t \\ &= \varepsilon_0 \underset{\sim}{\chi}^0 \hat{\mathscr{E}}_0 \cos \omega_0 t + \frac{1}{2} \varepsilon_0 \frac{\partial \underset{\sim}{\chi}^0}{\partial X} \; X_0 \hat{\mathscr{E}}_0 \{ \cos[\omega_0 + \omega(\boldsymbol{q})] t + \cos[\omega_0 - \omega(\boldsymbol{q})] t \} \, . \end{aligned} \tag{III.6}$$

The scattered radiation expressed by (III.4) therefore contains, along with the elastic contribution of frequency ω_0 (the Rayleigh scattering), further terms known as Raman side bands with the frequencies $\omega_0 \pm \omega(\boldsymbol{q})$ (Fig. III.1). The plus and minus signs correspond to scattered light quanta that have, respectively, absorbed the energy of, and lost energy to, the relevant elementary excitation $[\omega(q), \boldsymbol{q}]$. The lines with frequency smaller than ω_0 are called the Stokes lines; those with higher frequency are the anti-Stokes lines. For the latter lines to be present it is necessary that the elementary excitation, e.g. phonon, is already excited in the solid. Thus at low temperatures the intensity of the anti-Stokes lines is much reduced because the relevant elementary excitation is largely in its ground state. The intensity of the inelastically scattered radiation is typically a factor of 10^6 weaker than that of the primary radiation.

A prerequisite for the observation of a Raman line is that the susceptibility $\underset{\sim}{\chi}$ (III.5) has a non-vanishing derivative with respect to the coordinate X of the elementary excitation. On account of the crystal symmetry and the resulting symmetry properties of the elementary excitation that determine the vanishing or nonvanishing of the quantities $(\partial \chi_{ij} / \partial X)$, the observability of the corresponding Raman lines depends on the geometry of the experiment. This is illustrated for the example of two Raman spectra measured from a $\mathrm{Bi_2Se_3}$ single crystal (Fig. III.2). $\mathrm{Bi_2Se_3}$ possesses a trigonal c-axis along which the crystal is built up of layers of Bi and Se. This crystal symmetry means, among other things, that the normal susceptibility tensor has the following form when referred to the principal axes:

$$\underset{\sim}{\chi}^0 = \begin{bmatrix} \chi^0_{xx} & 0 & 0 \\ 0 & \chi^0_{xx} & 0 \\ 0 & 0 & \chi^0_{zz} \end{bmatrix} . \tag{III.7}$$

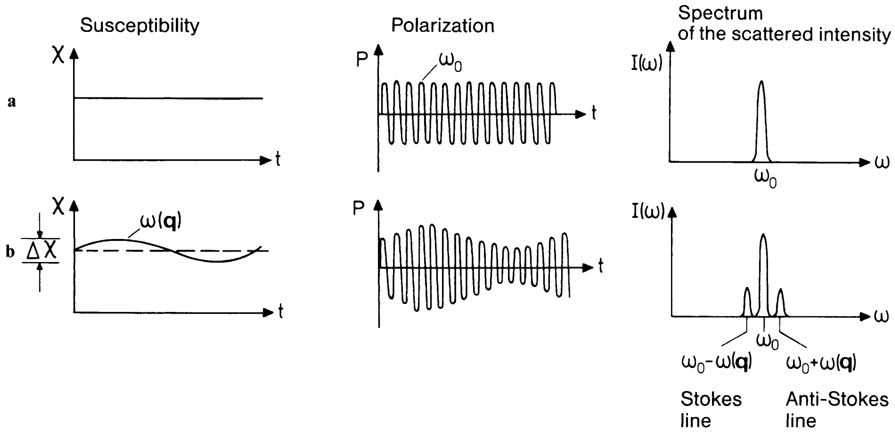


Fig. III.1. Schematic representation of the mechanisms of elastic (**a**) and inelastic (**b**) light scattering (Raman scattering): (**a**) if the electronic susceptibility is assumed to be constant in time, the polarization P oscillates with the frequency ω_0 of the incident light and, in turn, radiates only at this frequency (elastic process); (**b**) if the susceptibility itself oscillates with the frequency $\omega(\boldsymbol{q})$ of an elementary excitation (e.g. phonon), then the oscillation of the polarization induced by the primary radiation (frequency ω_0) is modulated with frequency $\omega(\boldsymbol{q})$. This modulated oscillation of the polarization leads to contributions in the scattered light from the so-called Raman side bands of frequencies $\omega_0 \pm \omega(\boldsymbol{q})$

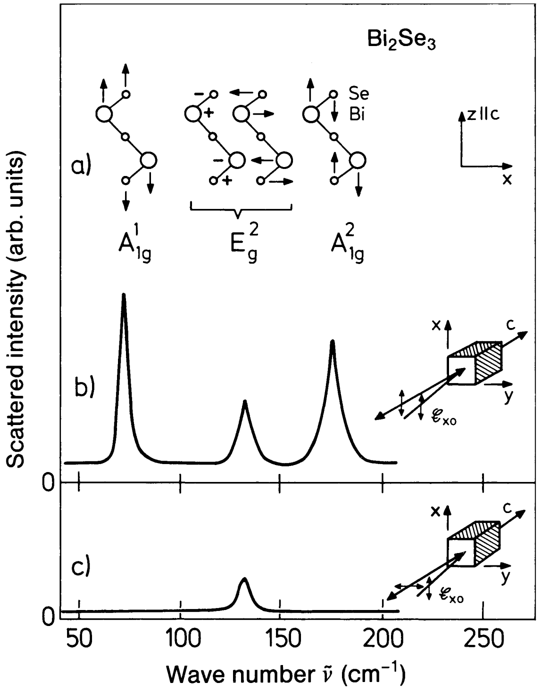


Fig. III.2 a–c. Raman spectra of phonons of types A_{1g} and E_g^2 measured from a single crystal of Bi_2Se_3. The c-axis of the crystal lies parallel to the z-axis of the coordinate system. (**a**) The displacement patterns of the A_{1g} and E_g^2 phonons for one of the three basis atom configurations in the nonprimitive unit cell. Arrows and +/– signs give a snapshot view of the atomic displacements. (**b**) Raman spectrum taken in the geometry $z(xx)\bar{z}$, i.e., the primary wave is incident in the z-direction and is polarized in the x-direction; the Raman scattered light is detected in the $-z$ (or $\bar{z}$) direction, and analysed for its x-polarized component. (**c**) Raman spectrum taken in the geometry $z(xy)\bar{z}$ [III.2]

In the measurements of Fig. III.2 the beam was incident along the c-axis (z-axis of the coordinate system), and the scattering was analyzed in the backscattering direction, i.e., also along the z-direction. If a polarization of the x-direction is present for both the incident and scattered radiation, then one will observe the phonons denoted by A^1_{1g}, A^2_{1g} and E^2_g (Fig. III.2b). If, however, one measures scattered light with a polarization in the y-direction, then only E^2_g will appear in the Raman spectrum (Fig. III.2c). This can be understood by considering the nature of the atomic displacements associated with the two types of phonon (Fig. III.2a): if a phonon of type A_{1g} is excited, the symmetry of the crystal remains unchanged; thus the change in the susceptibility χ_{ij} induced by the phonon displacement, i.e., $(\partial\chi_{ij}/\partial X)$ leads to a tensor that has the same form as χ^0_{ij} (III.7). Such a tensor implies that the polarization induced by the incident electric field $\mathscr{E}_0 = (\mathscr{E}_{x0}, \mathscr{E}_{y0}, 0)$, has the same direction as $\mathscr{E}_0$. In other words, for phonons of the type A_{1g} one has $(\partial\chi_{xy}/\partial X) = 0$.

According to Fig. III.2a, a general phonon of the type E_g possesses displacements in both the x- and y-directions. The trigonal crystal symmetry is therefore broken by this phonon. The phonon-induced modification of the susceptibility in the x-direction is coupled to a modification in the y-direction. An incident electric field $\mathscr{E}_{x0}$ thus induces polarization changes in both the x- and y-directions. The scattered light that results contains polarization components in both these directions, i.e., $(\partial\chi_{xx}/\partial X) \neq 0$, $(\partial\chi_{xy}/\partial X) \neq 0$.

For crystals with centers of inversion (e.g. the NaCl and CsCl structures) there is a general exclusion principle which states that infrared-active transverse optical (TO) phonons (Sects. 4.3, 11.3, 11.4) are not Raman active and vice versa.

As a further example of an experimental Raman spectrum, Fig. III.3 shows the spectrum measured for an n-doped GaAs crystal with a free electron density of $n = 10^{16}\,\mathrm{cm}^{-3}$ (Sect. 12.3). Besides the strong lines between wavenumbers 250 and $300\,\mathrm{cm}^{-1}$ (wavenumber $\tilde{\nu} = \lambda^{-1}$) attributable to the excitation of TO and LO phonons, one also observes a structure at $40\,\mathrm{cm}^{-1}$ very close to the elastic peak ($\tilde{\nu}=0$). This structure is essentially the result of excitation of collective vibrations of the "free" electron gas, so-called plasmons (Sect. 11.9). A weak coupling between the plasmons and the LO phonons leads to a small frequency shift in both these peaks.

Also of interest is the dependence of the Raman spectra on the primary energy $\hbar\omega_0$. If the incident photon energy $\hbar\omega_0$ is exactly equal to the energy of an electronic transition, i.e. if it corresponds to a resonance in χ or in the dielectric constant $\varepsilon(\omega)$, then one observes an enormous enhancement of the Raman scattering cross section, or so-called *resonant Raman scattering*. By varying the primary energy in order to find such resonances in the Raman cross section, it is also possible to study electronic transitions.

From (III.4) it follows that, for frequencies below the electronic resonance, the intensity varies as ω^4 or λ^{-4} as a function of the frequency or wavelength of the incident light; it is thus desirable to use as short a

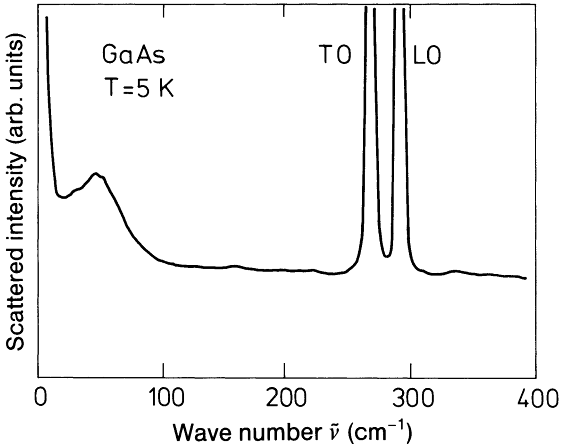


Fig. III.3. Raman spectrum of an *n*-doped GaAs crystal at a sample temperature of 5 K. The concentration of free electrons is $n \simeq 10^{16}\,\mathrm{cm}^{-3}$. TO and LO denote transverse and longitudinal optical phonons. The band at 40 cm^{-1} stems essentially from plasmon excitations [III.3]

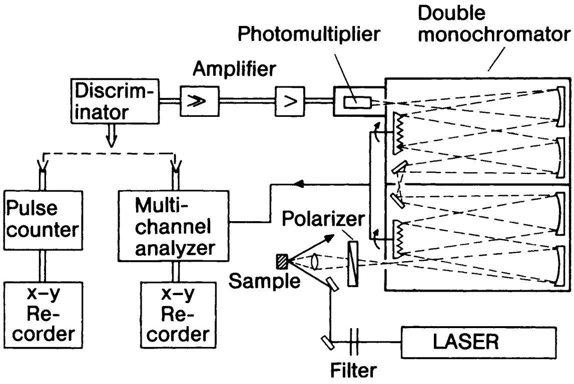


Fig. III.4. Schematic of experimental arrangement used to observe the Raman effect. To minimize the background due to internal scattering in the measuring device, a double monochromator is used. Furthermore, because of the weak signal a pulse counting technique is applied. The path of the Raman-scattered light is shown by the dashed lines

wavelength as possible. Today, high-power lasers (neodymium, krypton, argon-ion, etc.) are used for this purpose. For resonance Raman spectroscopy in particular one can employ tunable dye lasers. Emission powers of up to several watts in the violet and near-UV spectral range are applied. To detect the scattered radiation in the visible and near-UV one uses highly sensitive photomultipliers. High demands are made of the spectrometer used to analyse the scattered radiation: whereas the primary photon energy is in the range 2–4 eV, i.e. has a frequency ν of the order of 10^{15} Hz, one needs to measure frequency differences between this and the Raman side bands that lie anywhere from a few Hertz to 10^{14} Hz ($\widehat{=}\, 3000\,\mathrm{cm}^{-1}$). For scattering from sound waves in particular, a resolution of $\omega_0/\Delta\omega = 10^8$ is desirable. This can be achieved with Fabry-Pérot interferometers. In this case the method is commonly known as *Brillouin scattering*. Because of the low intensity of the Raman lines, it is important that there is no background intensity in the region close to primary line produced by primary light that has been scattered within the instrument, i.e. high contrast is an important prerequisite. Modern experiments often employ double or triple spectrometers (Fig. III.4). The gratings used are produced holographically in order to avoid spurious diffraction peaks (ghosts) in the spectral background intensity. Figure III.4 shows a modern experimental setup for Raman spectroscopy.

References

III.1 D. A. Long: *Raman Spectroscopy* (McGraw-Hill, New York 1977)
W. Hayes, R. Loudon: *Scattering of Light by Crystals* (Wiley, New York 1987)
III.2 W. Richter, H. Köhler, C. R. Becker: Phys. Status Solidi B 84, 619 (1977)
III.3 A. Mooradian: In: *Light Scattering Spectra of Solids*, ed. by G. B. Wright (Springer, Berlin Heidelberg 1969), p. 285