

2. Translational symmetry, reciprocal lattice, Brillouin zones, density of states

Invariance of infinite crystals with respect to translations (they form an Abelian group of symmetry operations)

$$\vec{T}_{\vec{n}} = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3, \quad n_1, n_2, n_3 \text{ integers.} \quad (1.1)$$

14 possible lattices (Bravais lattices). Combined with point symmetries - 7 systems, with a single or more types:

triclinic	(simple),
monoclinic	(simple, base centered),
orthorhombic	(simple; base centered, face centered, body centered),
tetragonal	(simple, base centered),
hexagonal	(simple),
rhombohedral	(simple),
cubic	(simple; face centered, body centered; abbreviations: SC, FCC, BCC).

For an overview of the 230 space groups, see https://en.wikipedia.org/wiki/Crystal_system:

<u>Crystal family</u>	<u>Crystal system</u>	<u>Required symmetries of the point group</u>	<u>Point groups</u>	<u>Space groups</u>	<u>Bravais lattices</u>	<u>Lattice system</u>
<u>Triclinic</u>	Triclinic	None	2	2	1	Triclinic
<u>Monoclinic</u>	Monoclinic	1 twofold <u>axis of rotation</u> or 1 <u>mirror plane</u>	3	13	2	Monoclinic
<u>Orthorhombic</u>	Orthorhombic	3 twofold axes of rotation or 1 twofold axis of rotation and 2 mirror planes	3	59	4	Orthorhombic
<u>Tetragonal</u>	Tetragonal	1 fourfold axis of rotation	7	68	2	Tetragonal
<u>Hexagonal</u>	Trigonal	1 threefold axis of rotation	5	7	1	Rhombohedral
	Hexagonal	1 sixfold axis of rotation		18		Hexagonal
<u>Cubic</u>	Cubic	4 threefold axes of rotation	7	27	3	Cubic
6	7	Total	32	230	14	7

The consequences of translational symmetry for the electron states

One-electron stationary states obey the Schroedinger equation

$$H\psi(\vec{r}) = \left[\frac{p^2}{2m} + V(\vec{r}) \right] \psi(\vec{r}) = \left[-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right] \psi(\vec{r}) = E\psi(\vec{r}) \quad (1.2)$$

with periodic potential V :

$$V(\vec{r} + \vec{T}_{\vec{n}}) = V(\vec{r}) . \quad (1.3)$$

Translations preserve Hamiltonian, probability density at the positions \vec{r} and $\vec{r} + \vec{T}_{\vec{n}}$ is the same,

$$|\psi(\vec{r} + \vec{T}_{\vec{n}})|^2 = |\psi(\vec{r}_{\vec{n}})|^2 . \quad (1.4)$$

Consequently, the wavefunction can differ by a complex factor of unite magnitude

$$C_{\vec{n}} = e^{i\phi(\vec{T}_{\vec{n}})} , \quad (1.5)$$

where φ is a scalar function of the vector argument. Performing two consecutive translations, $\vec{T}_{\vec{n}}$ and $\vec{T}_{\vec{m}}$, results in the multiplication of the wavefunction by the product $C_{\vec{m}}C_{\vec{n}}$, the function φ in Eq. (1.5) has to be a linear combination of the components of the translation vector, i.e., the scalar product

$$\varphi(\vec{T}_{\vec{n}}) = \vec{k} \cdot \vec{T}_{\vec{n}}. \quad (1.6)$$

Eigenfunctions of the Hamiltonian are therefore associated with vectors \vec{k} , guaranteeing the required properties with respect to the translations by the lattice vectors:

$$\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\vec{r}} u_{\vec{k}}(\vec{r}), \text{ where } u_{\vec{k}}(\vec{r} + \vec{T}_{\vec{n}}) = u_{\vec{k}}(\vec{r}). \quad (1.7)$$

This form is called Bloch function, factorized as the plane wave $e^{i\vec{k}\vec{r}}$ and the translationally invariant part u . The \vec{k} , vector, indexing the Bloch function, is not defined unambiguously. When adding a vector \vec{K} , which produces an integer multiple of 2π , in the scalar product of Eq. (1.6), the value of the phase factor $C_{\vec{n}}$ remains unchanged. Let us look for such vectors in the form of linear combinations of three vectors,

$$\vec{K}_{\vec{q}} = q_1 \vec{b}_1 + q_2 \vec{b}_2 + q_3 \vec{b}_3, \quad q_1, q_2, q_3 \text{ integers.} \quad (1.8)$$

The condition

$$\vec{K}_{\vec{q}} \cdot \vec{T}_{\vec{n}} = 2\pi m, \quad m \text{ integer}, \quad (1.9)$$

is fulfilled with

$$\vec{b}_1 = \frac{2\pi}{\Omega_0} \vec{a}_2 \times \vec{a}_3, \quad \vec{b}_2 = \frac{2\pi}{\Omega_0} \vec{a}_3 \times \vec{a}_1, \quad \vec{b}_3 = \frac{2\pi}{\Omega_0} \vec{a}_1 \times \vec{a}_2. \quad (1.10)$$

$\Omega_0 = \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)$ is the volume of primitive cell, based on the three vectors \mathbf{a} . Projections of individual vectors \mathbf{b} on the vectors \mathbf{a} of the same index amount to 2π , they vanish for different indices:

$$\vec{b}_q \cdot \vec{a}_n = 2\pi \delta_{qn}, \quad q, n = 1, 2, 3. \quad (1.11)$$

The set of vectors $\vec{K}_{\vec{q}}$ form the reciprocal lattice (the distances in the "reciprocal space" have the physical dimension of reciprocal length). The reciprocal lattice belongs to the same crystal system as the initial lattice in the direct space. The simple and base-centered type is also preserved, while the face- and body-centered types replace each other.

The \mathbf{k} -vectors in the Bloch functions are equivalent, whenever they differ by the vector of reciprocal lattice. We usually select them from the first Brillouin zone (this is the Wigner-Seitz cell of the reciprocal lattice):

we choose any of the lattice site as the origin, and draw planes perpendicular to the neighbors at half of their distance. The first Brillouine zone (1. BZ) is the volume inside the closest planes. The scalar products with primitive lattice vectors are within the interval of 2π , namely,

$$-\pi \leq \vec{k} \cdot \vec{a}_j \leq \pi, \quad j = 1, 2, 3. \quad (1.12)$$

The restriction to finite volume of a crystal is usually implied via the (cyclic) Born-Kármán conditions, repeating the wavefunctions at large distances:

$$\psi(\vec{r} + N_j \vec{a}_j) = \psi(\vec{r}), \quad j = 1, 2, 3, \quad (1.13)$$

where N_j are large positive integers. We expect the properties of such a crystal to be practically the same as those of a "sufficiently large" crystal, compared with inter-atomic distances. Pointing to these "bulk" properties, we evidently neglect the influence of surfaces and/or interfaces with different materials. This approximation usually fails for small crystals (crystallites, nanostructures).

The cyclic boundary conditions (1.13) imply the „quasicontinuum“ of possible \mathbf{k} -vectors within the first Brillouin zone. These are linear combinations of the primitive vectors of the reciprocal lattice,

$$\vec{k} = k_1 \vec{b}_1 + k_2 \vec{b}_2 + k_3 \vec{b}_3, \quad (1.14)$$

with the coefficients k_j from $-\frac{1}{2}$ to $\frac{1}{2}$ separated by the small step of $1/N_j$.

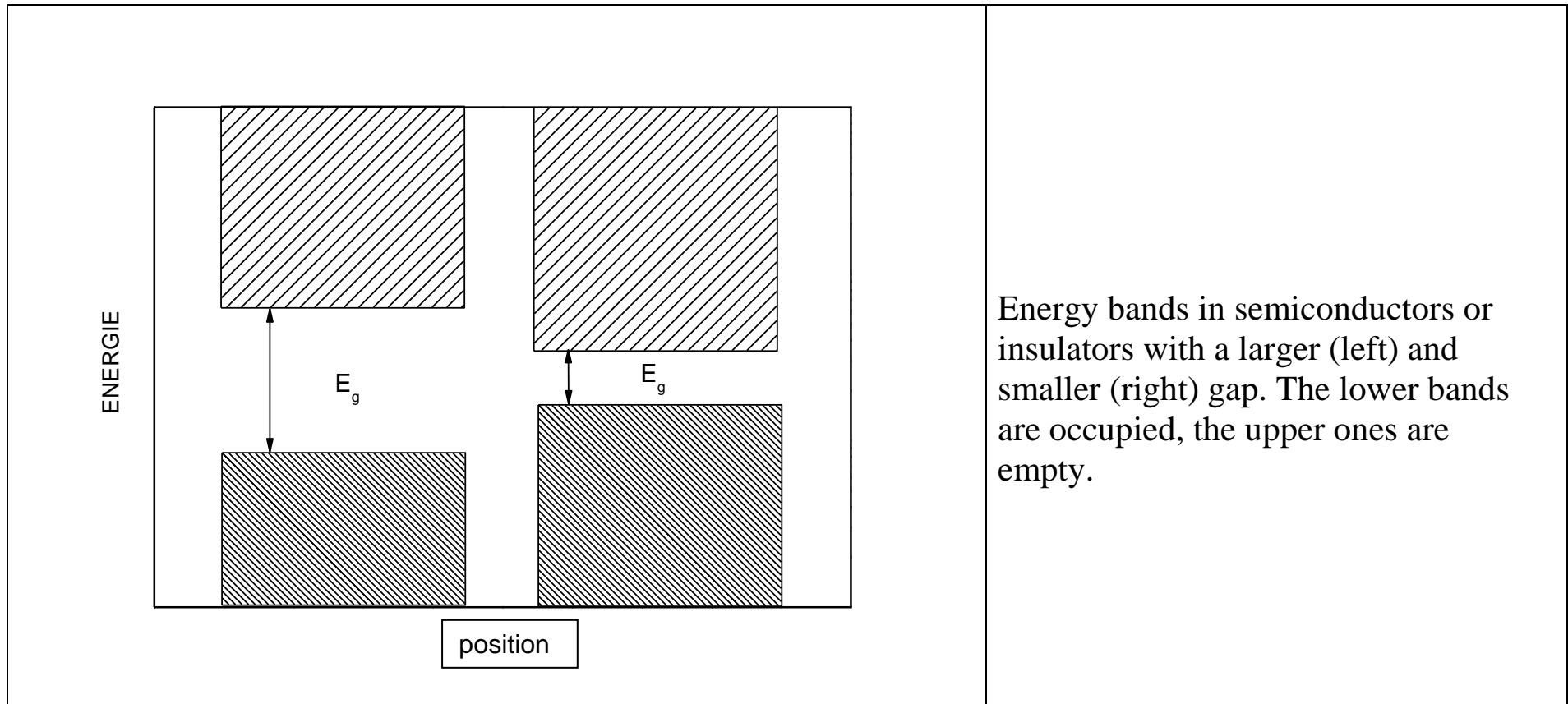
In the association of the stationary states of the one-electron Hamiltonian with the vector \mathbf{k} , we usually substitute the quasi-continuum of possible values by a continuum, and use differentiation with respect to its components and integration over them. Adding a further discrete index (quantum number) n , the Schrodinger equation (1.2) for the Bloch form of the wavefunction becomes

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + \frac{\hbar^2}{2m} |\vec{k}|^2 - i \frac{\hbar^2}{m} \vec{k} \cdot \nabla + V(\vec{r}) \right] e^{i\vec{k} \cdot \vec{r}} u_{\vec{k},n}(\vec{r}) = E_n(\vec{k}) e^{i\vec{k} \cdot \vec{r}} u_{\vec{k},n}(\vec{r}), \quad (1.15)$$

where we can remove the plane wave, $e^{i\vec{k} \cdot \vec{r}}$, obtaining the equation for the periodic part u . Its solutions can be limited to the primitive cell, with the boundary conditions provided by the periodicity of u .

(Quasi)continuous change of the eigenenergy E with changing the \mathbf{k} -vector within the 1. BZ and a given value of n is confined to an interval, denoted as n -th band; the dependence on the magnitude of \mathbf{k} along a given direction in the 1. BZ is called dispersion of energy in this direction. The set of bands of a given crystal is called bandstructure. The bandstructure can contain an interval with no allowed energies, called forbidden band, or gap. A rudimentary representation of bandstructure is the following:

energy



Energy bands in semiconductors or insulators with a larger (left) and smaller (right) gap. The lower bands are occupied, the upper ones are empty.

The occurrence of gap in semiconductors and insulators is substantial, making this way of depicting the bandstructure appropriate. For bulk material, using "position" in the crystal is irrelevant. However, in dealing with heterostructures (different materials connected with "atomic precision"), specifying the position is important. For example, we can idealize the heterostructures as being composed of different materials with distinct bandstructures. Their behavior is determined by the band alignment at interfaces; the upper figure

can represent one of the possible alignment of the occupied and free bands. The two materials can form a heterostructure described by a horizontal shift of the bandstructures until brought in contact.

Density of states

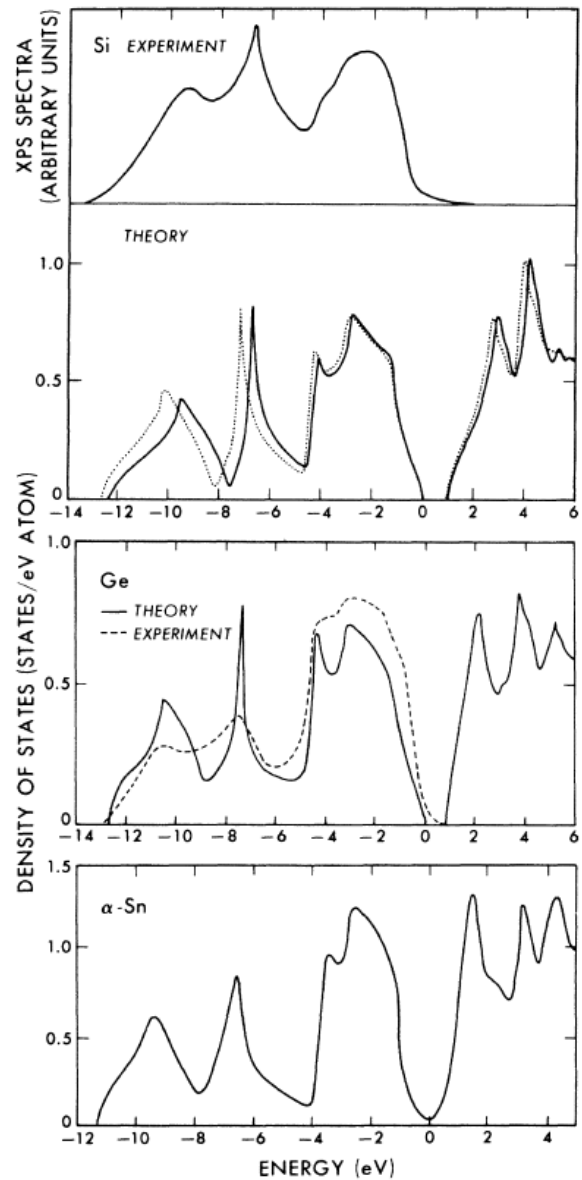
More complete information about the bandstructure is contained in the density of states, $D(E)$. The density is related to the energies, i.e., it represents the number of states, $P(E, E+dE)$, in the energy interval between E and $E+dE$, divided by the width of the interval, dE :

$$D(E) = \frac{P(E, E + dE)}{dE} . \quad (1.16)$$

Denoting by $N_n(E)$ the number of states from the lowest energy of the n -th band (a safe choice is $-\infty$) up to the argument E , we can utilize the (quasi)continuous intervals of the \mathbf{k} -vectors and energies E and produce the derivative of this function; the density of states results as the sum over all bands n :

$$D(E) = \sum_n D_n(E) = \sum_n \frac{dN_n(E)}{dE} . \quad (1.17)$$

Prototypical densities of states of Si, Ge and α -Sn (gray tin) are plotted in the following figure. We can reduce them to the simplest form by forming the occupied band from about -13 eV to zero for all of the three substances. Following this, we get the gap of about 1.2 eV (Si), 0.7 eV (Ge) and zero for α -Sn. Larger energies belong to the set of empty bands.



Density of states: calculated using nonlocal pseudopotentials, Chelikowsky and Cohen, PRB (1976). Experimental data from R. Pollak et al., PRL (1973) for Si, Grobman et al., PRL (1972) for Ge.

Equation (1.16) provides a convenient way of calculating the density of states. Since the allowed values of the \mathbf{k} -vector are equidistant, treating them as a quasicontinuum leads to the number $N_n(E)$ in the form of the volume limited by the area of $E_n(\mathbf{k}) = E$, divided by the volume belonging to a single state in the reciprocal space. Consequently, the contribution of the n-th band to the density of states results as the derivative of this ratio with respect to the energy E :

$$D_n(E) = \frac{d}{dE} \frac{\iiint_{E_n(\vec{k}) < E} d^3\vec{k}}{(2\pi)^3} = \frac{N_1 N_2 N_3 \Omega_0}{(2\pi)^3} \frac{d}{dE} \iiint_{E_n(\vec{k}) < E} d^3\vec{k} . \quad (1.18)$$

The volumes in reciprocal space can be calculated fairly easily for some of the dispersions of energy. A simple example is provided by the quadratic dispersion above a minimum band energy,

$$E_n(k_x, k_y, k_z) = E_0 + \frac{\hbar^2}{2} \left(\frac{k_x^2}{m_x^*} + \frac{k_y^2}{m_y^*} + \frac{k_z^2}{m_z^*} \right), \quad m_x^*, m_y^*, m_z^* > 0 . \quad (1.19)$$

This would be the dependence of energy of free electron on its momentum, if the effective masses m_x^*, m_y^*, m_z^* were independent of the direction, and equal to the mass of the electron in free space. The crystalline potential leads to the possibility of the inertia of electrons differ in different directions, and differ from the

free electron case. The equi-energy areas for the dispersion of Eq. (1.19) are ellipsoids, with volumes calculated easily using the transformed coordinates in the reciprocal space,

$$k'_j = \frac{k_j}{\sqrt{m_j^*}}, j = x, y, z, d^3\vec{k} = \sqrt{m_x^* m_y^* m_z^*} d^3\vec{k}' . \quad (1.20)$$

The volume integral in Eq. (1.18) is the volume of 3-dimensional sphere of the squared radius of $2(E-E_0)/\hbar^2$, amounting to $(4/3)\pi[2(E-E_0)/\hbar^2]^{3/2}$. The differentiation with respect to E leads to the contribution of the band (1.19) to the density of states in the form

$$D_n(E) = \frac{4\pi\sqrt{2}N_1N_2N_3\Omega_0}{(2\pi\hbar)^3} \sqrt{m_x^* m_y^* m_z^*} \sqrt{E - E_0} \text{ pro } E > E_0. \quad (1.18)$$

For energies below E_0 , the density of states vanishes (there are no states in such a band).

The parabolic dispersion occurs for free electrons, where the three effective masses are the same and equal to the fundamental physical constant m_0 . The system of free (noninteracting) electrons can be placed in a infinitely weak periodic potential, which does not change the dispersion relations; however, the symmetry of the potential matters, and we arrive at the concept of "empty lattice".

Empty FCC lattice, respecting the symmetry of its potential, leads to the band structure depicted in the following figure:

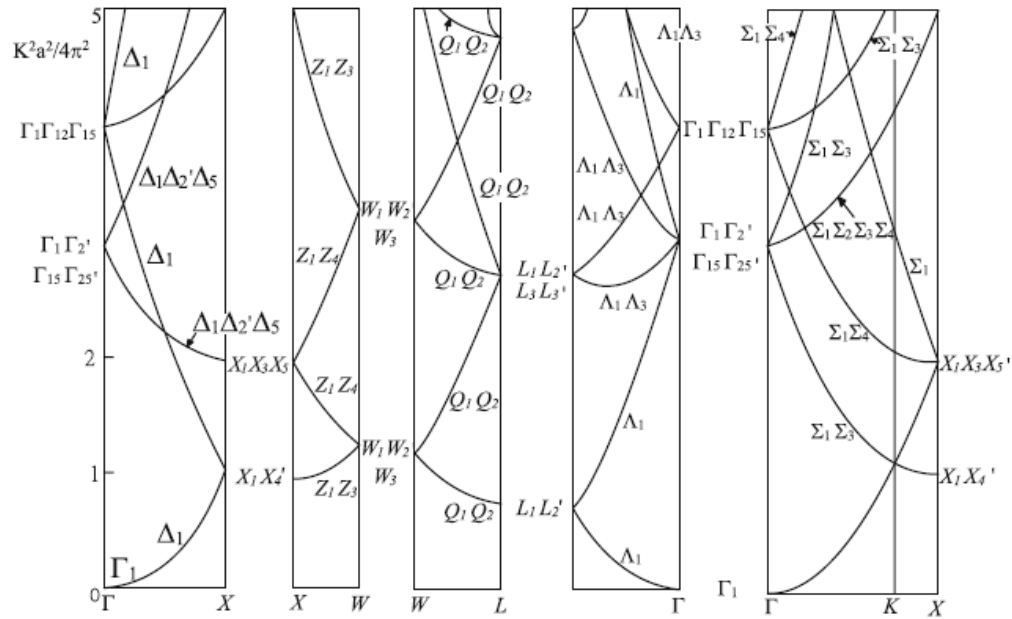
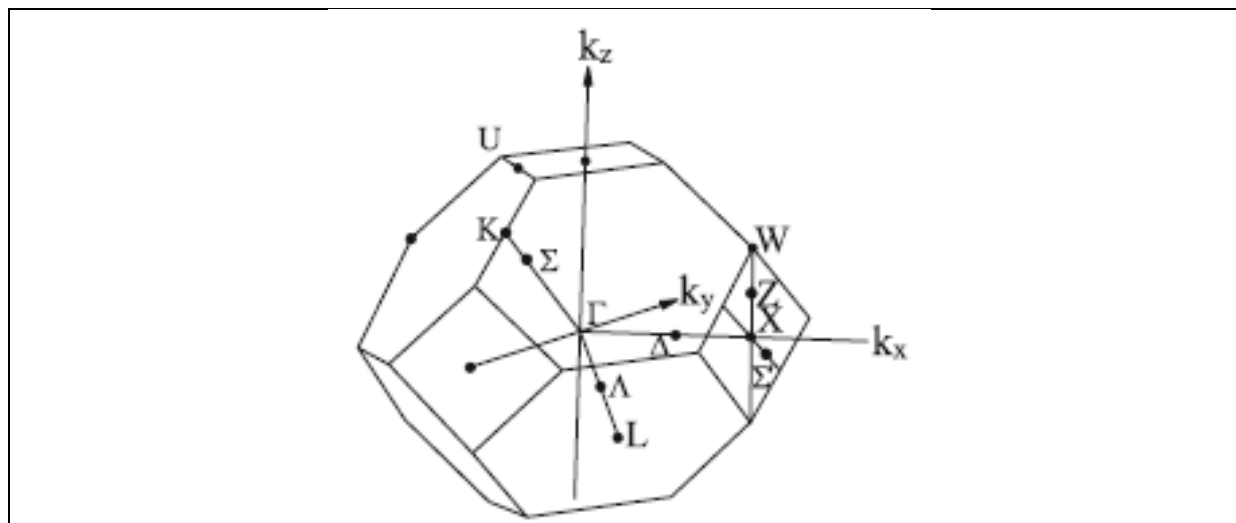


Fig. 12.1. Free-electron bands of the empty lattice in a face centered cubic structure. The labels of the high symmetry points in the FCC structure are given in Fig. C.5(a) of Appendix C. The band degeneracies can be obtained from the dimensions of the irreducible representations indicated on this diagram, and the energy is given in units of $(\hbar^2/2m)(2\pi/a)^2$

Bandstructure of the empty FCC lattice,
 from
 Dresselhaus, Dresselhaus & Jorio,
 Group Theory, Application to the
 Physics of Condensed Matter.

Standard symbols are used for the points and directions of high symmetry (this is the usual notation of irreducible representation of the corresponding symmetry group):



Symbols for the 1. BZ of the FCC structure.

What is the density of states for the empty FCC lattice?

Density of vibrational states; example of phonon dispersion of hexagonal SiC:

13 404

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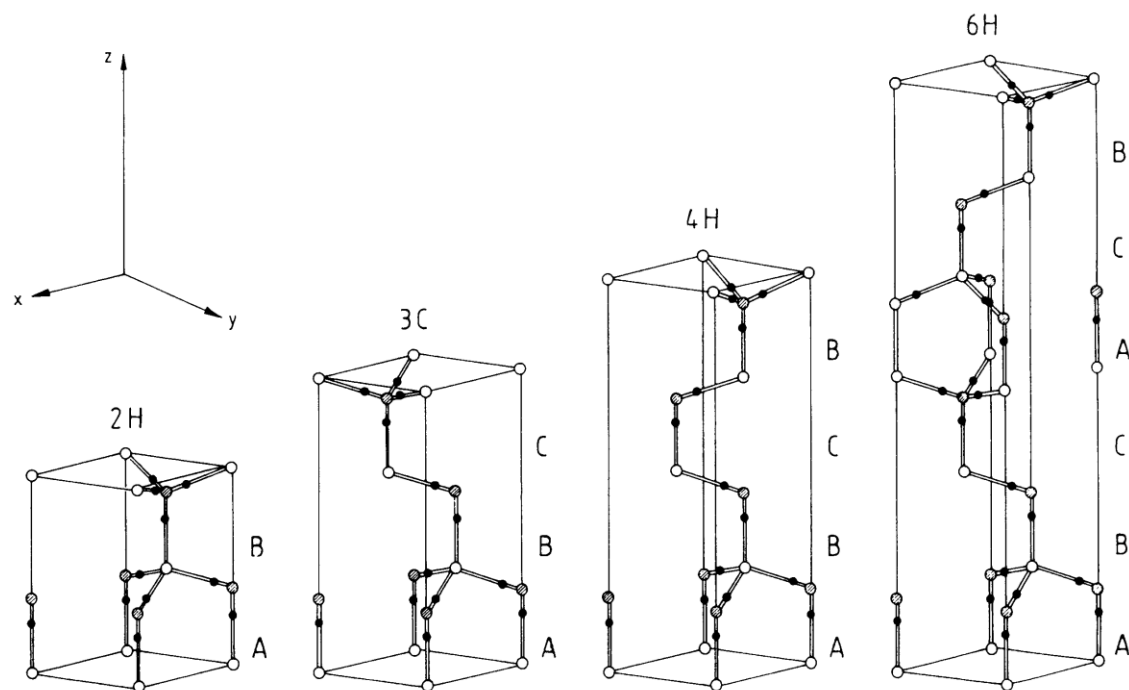


FIG. 2. Unit cells of the hexagonal SiC polytypes $2H$, $4H$, and $6H$. For completeness the $3C$ structure is also drawn in a hexagonal cell. Furthermore, the stacking sequences AB , ABC , $ABCB$, and $ABCACB$ are indicated. Si atoms are denoted by open circles, C atoms by hatched circles, and bond charges by dots.

Hoffmann et al., 1994.

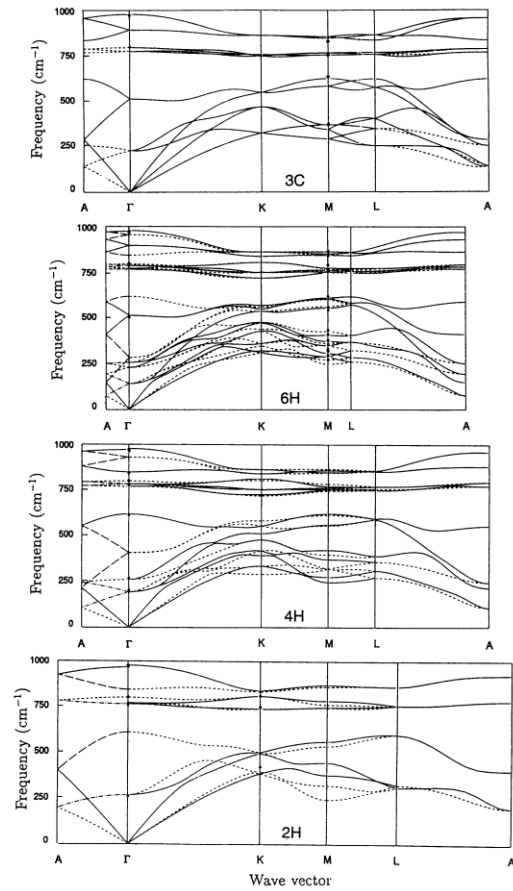


FIG. 4. Phonon dispersion curves for the $2H$ -, $3C$ -, $4H$ -, and $6H$ -SiC polytypes along high-symmetry lines in the hexagonal Brillouin zone. The experimental data from Tables I and II are represented by circles, triangles, and crosses. At the M point of the $6H$ structure additional experimental frequencies from Ref. 38 are also indicated. Solid, short-dashed, long-dashed, and dot-dashed lines indicate different polarization states. Their classification follows the transformation behavior of the phonon eigenvectors with the point-group operations.

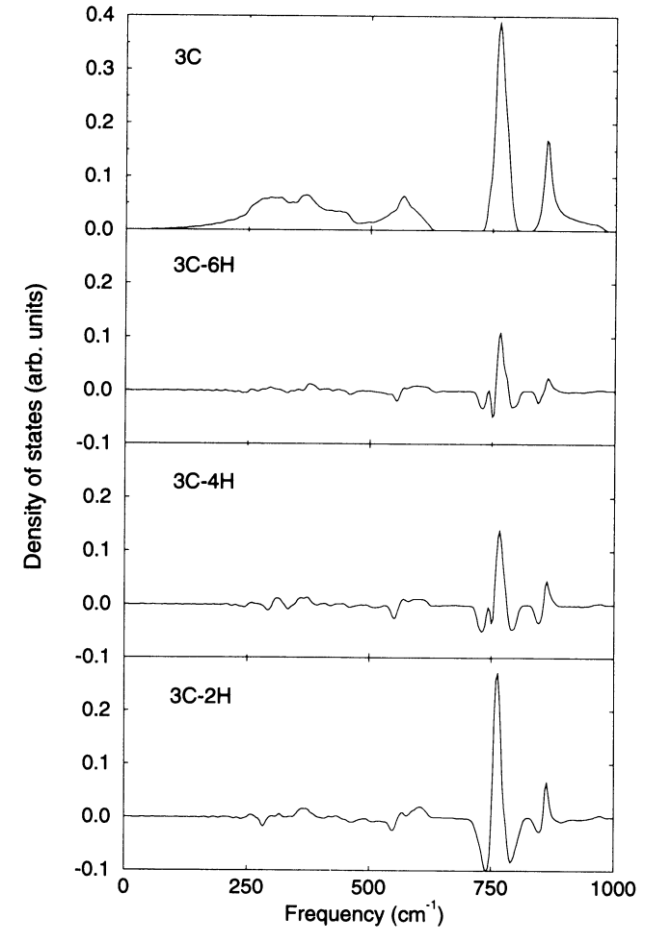


FIG. 5. Density of states of the four polytypes under consideration. Whereas the total one is plotted for $3C$ -SiC (uppermost panel), only the deviations from this one are shown for the hexagonal structures $6H$, $4H$, and $2H$ (lower panels).