Structure of solids

Solids are either amorphous or crystalline in structure, in many cases partial- crystalline.
Crystals are homogeneous (in matter) and anisotropic (in physical properties) solids.
They are characterised by translational symmetry

$$\vec{r} = m_1 \vec{a}_1 + m_2 \vec{a}_2 + m_3 \vec{a}_3 \quad \text{where } m_i = \text{integer numbers, } \vec{a}_i \text{ basis vectors}$$

Each point in an infinite crystal can be reached by symmetry operations such as translation, mirror planes, and 1,2,3,4 or 6 fold rotational axes. 5-fold or axes higher than 6 are impossible in homogeneous crystals, (but possible in “quasi-crystals”). Each crystal is composed by an infinite repetition of a unit cell in all three dimension of space. Note: the surface breaks this symmetry.
All crystals can be classified into 7 crystal systems: triklin, monoklin, orthorhombic, tetragonal, trigonal (rhombohedral), hexagonal and cubic.
The anisotropy of the crystal’s properties is completely determined by the symmetry of the respective crystal. On the other hand the choice of the unit cell is arbitrary. By convention the unit cell should consider (a) the complete symmetry of the whole crystal and (b) minimum number of atoms (molecules) within the unit cell.

Considering these requirements, complete filling of the 3D space by appropriate unit cells results in 14 Bravais lattices. The cubic system is compatible with 3 such Bravais lattices: cubic primitive (one atom), body centred cubic – bcc (2 atoms) and face centred cubic – fcc (4 atoms per unit cell). In the tetragonal system, “fcc” is not necessary due to symmetry.

The fcc lattice and hexagonal lattice – hcp – can be described by a stacking of 2D planes made up by dense packed rigid spheres: dense packing = „dichteste Kugelpackung“ → stacking in ABAB sequence results in hcp → stacking in ABCABC... → fcc. Both fcc and hcp are the most dense packed structures in nature. Most of the elements crystallize in fcc, hcp or bcc lattices.
The lattice of many chemical compounds can be described by certain composition of these three Bravais lattices:
i.e. NaCl : Na -> fcc with origin in (0 0 0) , Cl → fcc with origin in (½ 0 0)
ZnSe : Zn → fcc with origin in (0 0 0) , Se →fcc with origin in (¼ ¼ ¼)

The Reciprocal lattice is related to the periodicity of the crystal lattice and can be considered as it’s Fourier-transformation. The basis vectors $\mathbf{b}_i$ of the reciprocal lattice are related to the basis vectors $\mathbf{a}_i$ of real space by the relation

$$b_i = 2\pi\,\varepsilon_{ijk}\,\frac{a_j \times a_k}{a_i \cdot a_j \times a_k}$$

The experiment of Laue, Friedrich and Knipping in 1912 was the beginning of modern solid state physics and crystallography. The Laue pattern has been interpreted by interference of an x-ray wave at a 3D periodic lattice of atoms within the crystal. For the case of orthorhombic crystal lattice the Laue equations are:

$$\cos\alpha - \cos\alpha_0 = \frac{N_x \lambda}{a}$$

$$\cos\beta - \cos\beta_0 = \frac{N_y \lambda}{b} \qquad \text{resulting in the condition:} \quad \lambda = \frac{2\frac{N_z}{c}}{\frac{N_x^2}{a^2} + \frac{N_y^2}{b^2} + \frac{N_z^2}{c^2}}$$

$$\cos\gamma - \cos\gamma_0 = \frac{N_z \lambda}{c}$$

That means distict Laue peaks appear only for certain ratio between wave length and lattice parameters.
The Laue experiment has verified the wave character of x-rays and that a crystalline solid is composed by a 3D periodic arrangement of atoms. Max von Laue has explained the appearance of discrete spots in a diffraction pattern by the interference of x-ray induced fluorescence emitted by the atom which was not correct. End of 1912 William Lawrence Bragg explained the appearance of these peaks by diffraction at crystal lattice planes. The Bragg equation

$$\lambda = 2d(hkl)\sin\theta$$

presents a relation between the lattice distance *d(hkl)* of the diffracting lattice plane and the diffraction angle θ. λ is the wave length. *hkl* are the Miller indices. The vector

$$\vec{K} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3 = [hkl]$$

is the normal of the diffracting lattice plane indexed by (*hkl*). In kinematic theory (diffraction at small crystals) the intensity of a Bragg reflection (see Laue Interference) is proportional to the size of a small crystal S^2

$$I \approx S^2(N_1N_2N_3) = |\sum_i \frac{\sin(0.5N_i a_i)}{\sin(0.5a_i)}|^2$$

where N_i are the number of unit cell along a_i. In addition I is proportional to the square of the structure factors F:

$$I(hkl) \approx |F|^2 = |\sum_n f_n \exp(-2\pi i(hx_i + ky_i + lz_i)|^2$$

where x_i, y_i z_i are the relative coordinates of atoms within the unit cell,

The relative positions	in bcc are	(0,0,0) + (½ ½ ½); :
	in fcc are	(0,0,0) , (½ ½ 0) , (½ 0 ½) , (0 ½ ½),
	in hcp are	(0 0 0) , (1/3 2/3 ½).

Depending on the Bravais lattice type and indices *hkl*, the intensity of a certain Bragg reflection may become zero (extinction) although the Bragg equation is fulfilled. This extinction rules allow the identification of the crystal structure by x-ray diffraction→ x-ray crystal structure analysis.