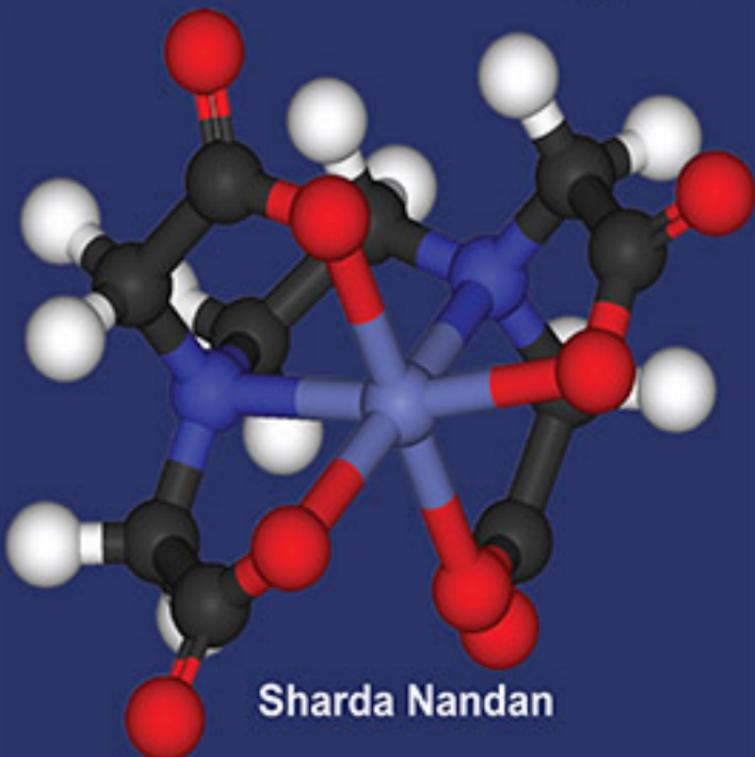




Solid State Chemistry



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Sharda Nandan

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Preface

The field of solid state and materials chemistry has grown significantly over the last two decades with successes in the preparation of new materials with unique electronic, optical, magnetic and catalytic properties. These materials provide the foundation, while structure-property correlations provide the framework for existing and emerging technologies.

Solid-state chemistry, also sometimes referred to as materials chemistry, is the study of the synthesis, structure, and properties of solid phase materials, particularly, but not necessarily exclusively of, non-molecular solids. It therefore has a strong overlap with solid-state physics, mineralogy, crystallography, ceramics, metallurgy, thermodynamics, materials science and electronics with a focus on the synthesis of novel materials and their characterization.

The scope and importance of solid-state chemistry has grown not only with the discovery of new materials but also through the advancement of techniques for preparing and studying them, and in advanced computational predictions for structures and properties. Our knowledge of the diverse properties of solids continues to expand.

The goal of this book is that it should be easily accessible to undergraduates and other level of students.

—Editor

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Crystal Systems

The crystal systems are a grouping of crystal structures according to the axial system used to describe their lattice. Each crystal system consists of a set of three axes in a particular geometrical arrangement. There are seven unique crystal systems. The simplest and most symmetric, the cubic (or isometric) system, has the symmetry of a cube, that is, it exhibits four threefold rotational axes oriented at 109.5 degrees (the tetrahedral angle) with respect to each other. These threefold axes lie along the body diagonals of the cube. This definition of a cubic is correct, although many textbooks incorrectly state that a cube is defined by three mutually perpendicular axes of equal length – if this were true there would be far more than 14 Bravais lattices. The other six systems, in order of decreasing symmetry, are hexagonal, tetragonal, rhombohedral (also known as trigonal), orthorhombic, monoclinic and triclinic. Some crystallographers consider the hexagonal crystal system not to be its own crystal system, but instead a part of the trigonal crystal system. The crystal system and Bravais lattice of a crystal describe the (purely) translational symmetry of the crystal.

POINT AND SPACE GROUPS

The crystallographic point group or crystal class is the mathematical group comprising the symmetry operations that

leave at least one point unmoved and that leave the appearance of the crystal structure unchanged.

These symmetry operations can include reflection, which reflects the structure across a reflection plane, rotation, which rotates the structure a specified portion of a circle about a rotation axis, inversion which changes the sign of the coordinate of each point with respect to a centre of symmetry or inversion point and improper rotation, which consists of a rotation about an axis followed by an inversion.

Rotation axes (proper and improper), reflection planes, and centers of symmetry are collectively called symmetry elements. There are 32 possible crystal classes. Each one can be classified into one of the seven crystal systems.

The space group of the crystal structure is composed of the translational symmetry operations in addition to the operations of the point group.

These include pure translations which move a point along a vector, screw axes, which rotate a point around an axis while translating parallel to the axis, and glide planes, which reflect a point through a plane while translating it parallel to the plane. There are 230 distinct space groups.

ADVANTAGES OF A CRYSTAL

In principle, an atomic structure could be determined from applying X-ray scattering to non-crystalline samples, even to a single molecule. However, crystals offer a much stronger signal due to their periodicity.

A crystalline sample is by definition periodic; a crystal is composed of many unit cells repeated indefinitely in three independent directions. Such periodic systems have a Fourier transform that is concentrated at periodically repeating points in reciprocal space known as Bragg peaks; the Bragg peaks correspond to the reflection spots observed in the diffraction image.

Since the amplitude at these reflections grows linearly with the number N of scatterers, the observed intensity of these

spots should grow quadratically, like N^2 . In other words, using a crystal concentrates the weak scattering of the individual unit cells into a much more powerful, coherent reflection that can be observed above the noise. This is an example of constructive interference.

In a non-crystalline sample, molecules within that sample would be in random orientations and therefore would have a continuous Fourier spectrum that spreads its amplitude more uniformly and with a much reduced intensity, as is observed in SAXS. More importantly, the orientational information is lost. In the crystal, the molecules adopt the same orientation within the crystal, whereas in a liquid, powder or amorphous state, the observed signal is averaged over the possible orientations of the molecules.

Although theoretically possible with sufficiently low-noise data, it is generally difficult to obtain atomic-resolution structures of complicated, asymmetric molecules from such rotationally averaged scattering data. An intermediate case is fibre diffraction in which the subunits are arranged periodically in at least one dimension.

BAND STRUCTURE OF CRYSTALS

Brillouin Zone

Because electron momentum is the reciprocal of space, the dispersion relation between the energy and momentum of electrons can best be described in reciprocal space. It turns out that for crystalline structures, the dispersion relation of the electrons is periodic, and that the Brillouin zone is the smallest repeating space within this periodic structure. For an infinitely large crystal, if the dispersion relation for an electron is defined throughout the Brillouin zone, then it is defined throughout the entire reciprocal space.

Theory of band structures

The ansatz is the special case of electron waves in a periodic crystal lattice using Bloch waves as treated generally in the

dynamical theory of diffraction. Every crystal is a periodic structure which can be characterized by a Bravais lattice, and for each Bravais lattice we can determine the reciprocal lattice, which encapsulates the periodicity in a set of three reciprocal lattice vectors (b_1, b_2, b_3).

Now, any periodic potential $V(r)$ which shares the same periodicity as the direct lattice can be expanded out as a Fourier series whose only non-vanishing components are those associated with the reciprocal lattice vectors.

So the expansion can be written as:

$$V(r) = \sum_K V_k e^{iK.r}$$

where $K = m_1 b_1 + m_2 b_2 + m_3 b_3$ for any set of integers (m_1, m_2, m_3).

From this theory, an attempt can be made to predict the band structure of a particular material, however most ab initio methods for electronic structure calculations fail to predict the observed band gap.

Nearly-free Electron Approximation

In the nearly-free electron approximation in solid state physics interactions between electrons are completely ignored. This approximation allows use of Bloch's Theorem which states that electrons in a periodic potential have wavefunctions and energies which are periodic in wavevector up to a constant phase shift between neighboring reciprocal lattice vectors.

The consequences of periodicity are described mathematically by the Bloch wavefunction:

$$Y_{n,k}(r) = e^{ik.r} u_n(r)$$

where the function $u_n(r)$ is periodic over the crystal lattice, that is,

$$u_n(r) = u_n(r - R).$$

Here index n refers to the n-th energy band, wavevector k is related to the direction of motion of the electron, r is position in the crystal, and R is location of an atomic site.

Tight-binding Model

The opposite extreme to the nearly-free electron approximation assumes the electrons in the crystal behave much like an assembly of constituent atoms. This tight-binding model assumes the solution to the time-independent single electron Schrödinger equation \mathcal{O} is well approximated by a linear combination of atomic orbitals $\psi_n(r)$.

$$Y(r) = \sum_{n,R} b_{n,R} \psi_n(r - R),$$

where the coefficients $b_{n,R}$ are selected to give the best approximate solution of this form. Index n refers to an atomic energy level and R refers to an atomic site. A more accurate approach using this idea employs Wannier functions, defined by,

$$a_n(r - R) = \frac{V_C}{(2\pi)^3} \int_{BZ} dk e^{-ik.(R-r)} u_{nk};$$

in which u_{nk} is the periodic part of the Bloch wave and the integral is over the Brillouin zone. Here index n refers to the n-th energy band in the crystal. The Wannier functions are localized near atomic sites, like atomic orbitals, but being defined in terms of Bloch functions they are accurately related to solutions based upon the crystal potential. Wannier functions on different atomic sites R are orthogonal. The Wannier functions can be used to form the Schrödinger solution for the n-th energy band as:

$$Y_{n,k}(r) = \sum_R e^{-ik.(R-r)} a_n(r - R)$$

Ab initio Density-functional Theory

In present days physics literature, the large majority of the electronic structures and band plots is calculated using the density-functional theory (DFT) which is not a model but rather an ab initio theory, i.e. a microscopic first-principle theory of condensed matter physics that tries to cope with the electron-electron many-body problem via the introduction of an exchange-correlation term in the functional of the electronic density. DFT calculated bands are found in many cases in agreement with experimental measured bands, for example by

angle-resolved photoemission spectroscopy (ARPES). In particular, the band shape seems well reproduced by DFT. But also there are systematic errors of DFT bands with respect to the experiment. In particular, DFT seems to underestimate systematically by a 30-40% the band gap in insulators and semiconductors.

It must be said that DFT is in principle an exact theory to reproduce and predict ground state properties (e.g. the total energy, the atomic structure, etc.).

However DFT is not a theory to address excited state properties, such as the band plot of a solid that represents the excitation energies of electrons injected or removed from the system.

What in literature is quoted as a DFT band plot is a representation of the DFT Kohn-Sham energies, that is the energies of a fictive non-interacting system, the Kohn-Sham system, which has no physical interpretation at all.

The Kohn-Sham electronic structure must not be confused with the real, quasiparticle electronic structure of a system, and there is no Koopman's theorem holding for Kohn-Sham energies, like on the other hand for Hartree-Fock energies that can be truly considered as an approximation for quasiparticle energies. Hence in principle DFT is not a band theory, not a theory suitable to calculate bands and band-plots.

Green's Function

To calculate the bands including electron-electron interaction many-body effects, one can resort to so called Green's function methods. Indeed, the knowledge of the Green's function of a system provides both ground (the total energy) and also excited state observables of the system. The poles of the Green's function are the quasiparticle energies, the bands of a solid. The Green's function can be calculated by solving the Dyson equation once the self-energy of the system is known. For real systems like solids, the self-energy is a very complex quantity and usually approximations are needed to solve the problem.

One of such approximations is the GW approximation, so called from the mathematical form the self-energy takes as product $\hat{O} = GW$ of the Green's function G and the dynamically screened interaction W .

This approach is more pertinent to address the calculation of band plots (and also quantities beyond, such as the spectral function) and can be also formulated in a completely ab initio way. The GW approximation seems to provide band gaps of insulators and semiconductors in agreement with the experiment and hence to correct the systematic DFT underestimation.

Mott Insulators

Although the nearly-free electron approximation is able to describe many properties of electron band structures, one consequence of this theory is that it predicts the same number of electrons in each unit cell. If the number of electrons is odd, we would then expect that there is an unpaired electron in each unit cell, and thus that the valence band is not fully occupied, making the material a conductor.

However, materials such as CoO that have an odd number of electrons per unit cell are insulators, in direct conflict with this result. This kind of material is known as a Mott insulator, and requires inclusion of detailed electron-electron interactions (treated only as an averaged effect on the crystal potential in band theory) to explain the discrepancy. The Hubbard model is an approximate theory that can include these interactions.

PHYSICAL PROPERTIES AND IMPURITIES IN CRYSTALS

Real crystals feature defects or irregularities in the ideal arrangements described above and it is these defects that critically determine many of the electrical and mechanical properties of real materials.

When one atom substitutes for one of the principal atomic components within the crystal structure, alteration in the

electrical and thermal properties of the material may ensue. Impurities may also manifest as spin impurities in certain materials.

Research on magnetic impurities demonstrates that substantial alteration of certain properties such as specific heat may be affected by small concentrations of an impurity, as for example impurities in semiconducting ferromagnetic alloys may lead to different properties as first predicted in the late 1960s.

Dislocations in the crystal lattice allow shear at lower stress than that needed for a perfect crystal structure.

CRYSTALLOGRAPHY AND CRYSTAL DEFECTS

A plane of atoms can glide rigidly over its neighbour in process described as slip with the slip system defined by the plane and the direction of slip. This kind of deformation requires enormous stresses, far greater than those required to actually deform a crystal.

This is because almost all crystals contain defects known as dislocations. A dislocation enables the planes to glide in a piecewise manner rather than the rigid displacement of the entire plane.

This greatly reduces the stress required to cause slip. A good analogy to illustrate the role of a dislocation is to imagine the force required to pull an entire carpet along the floor. On the other hand, if a bump is introduced into the carpet, the force needed to move the bump along is much smaller.

The amount and direction of displacement produced by propagating the bump is, in the context of a dislocation, known as its Burgers vector.

Crystals may also contain point defects, which are imperfections of occupation. A vacancy is when an atom is missing from a site which should be occupied. An interstitial occurs when an atom is forced into a space within the crystal structure, where atoms are not normally located. Polycrystalline materials contain many crystals; another

common term for crystals in such materials is grains. Atoms in the grain boundary between crystals must in general be displaced from positions they would occupy in the undisturbed crystal. Therefore, grain boundaries are defects.

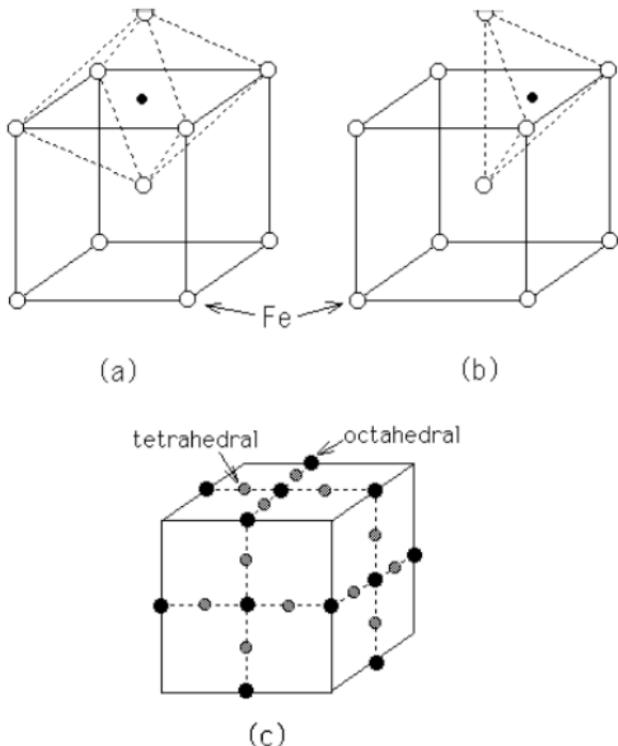


Fig. The Main Interstices in the Body-centred Cubic Structure of Ferrite. (a) An Octahedral Interstice; (b) A Tetrahedral Interstice; (c) Location of both kinds of Interstices.

CRYSTAL SYMMETRY PROPERTIES

Twenty of the 32 crystal classes are so-called piezoelectric, and crystals belonging to one of these classes (point groups) display piezoelectricity. All 21 piezoelectric classes lack a centre of symmetry.

Any material develops a dielectric polarization when an electric field is applied, but a substance which has such a natural charge separation even in the absence of a field is called

a polar material. Whether or not a material is polar is determined solely by its crystal structure. Only 10 of the 32 point groups are polar. All polar crystals are pyroelectric, so the 10 polar crystal classes are sometimes referred to as the pyroelectric classes.

There are a few crystal structures, notably the perovskite structure, which exhibit ferroelectric behaviour. This is analogous to ferromagnetism, in that, in the absence of an electric field during production, the ferroelectric crystal does not exhibit a polarisation. Upon the application of an electric field of sufficient magnitude, the crystal becomes permanently polarised.

This polarisation can be reversed by a sufficiently large counter-charge, in the same way that a ferromagnet can be reversed.

However, it is important to note that, although they are called ferroelectrics, the effect is due to the crystal structure, not the presence of a ferrous metal. the angle between the normals to the two intersecting faces is called interfacial angle.

Incommensurate crystals have period-varying translational symmetry. The period between nodes of symmetry is constant in most crystals. The distance between nodes in an incommensurate crystal is dependent on the number of nodes between it and the base node.

Interstices

The atoms inside a unit cell do not fill all space. The empty space represents the interstices. It is often the case that these interstices can accommodate small impurity atoms.

As an example, we shall consider the crystal structure of iron which at ambient temperature has the cubic-I lattice with an atom of iron at each lattice point. There are two kinds of interstitial sites capable of accommodating small atoms such as carbon or nitrogen. These are the tetrahedral and octahedral sites as illustrated.

IONIC RADII AND CRYSTAL STRUCTURE

The binding force in the majority of inorganic crystals is predominantly ionic in character. Moreover, since coulombic forces are spatially undirected, the sizes of the ions are important factors in determining the structure of crystals. Numerous attempts have been made to calculate a reliable set of ionic radii, from which ionic distances might be estimated with a fair degree of accuracy.

A crystal structure is largely determined by the ratio of the ionic radii of its components, and this ratio also regulates the coordination number of the smaller ion. In an ionic crystal each ion tends to surround itself with as many oppositely charged ions as possible, and the *number of nearest neighbours is the coordination number of the central ion*. When two oppositely charged ions are brought together, they are attracted to each other by coulombic forces; but as they approach close to one another, the electrostatic force is counteracted by a repulsive force developed between the two electronic systems.

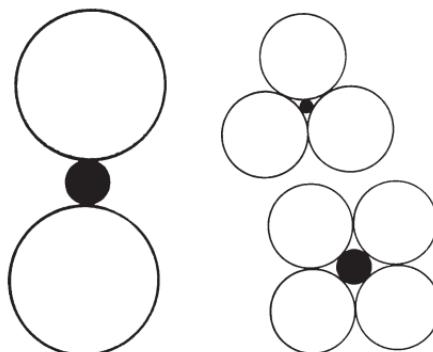
The ionic radii which have been assigned to ions from X-ray measurements are not actual radii but are instead the effective radii of the ions when packed together in a crystal.

Ionic distances are always fractions of interionic distances and are so chosen that they may be used to predict other interionic distances in other crystals.

It is usually assumed that the ions in a crystal are in bare contact with each other, but this assumption is not necessarily true. For convenience, ions are considered as rigid spheres; however, neither ions nor atoms have fixed surfaces, since the electron clouds of these particles may be constantly expanding and contracting and these clouds are certainly sometimes distorted by contact with other charged bodies.

The number of nearest neighbours is called the coordination number of an ion, and this number is dependent upon the radii of the ions, the radius ratio of the two ions, and the deformation of the ions as a result of size and charge. If we ignore the fact that ions may be deformed under the influence of surrounding

ions, and if we consider them to be perfect spheres, it is possible to determine the geometric pattern formed by two different ions in a crystal which will satisfy both the spatial and coulombic-force requirements.



Twofold Coordination

Threefold Coordination

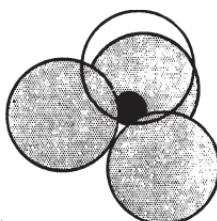


Fig: Fourfold Coordination Planar Fourfold Coordination Tetrahedral Coordination Number and the Relative Radii of Ions.

Assuming that ions are perfect spheres, it is possible to calculate, from geometrical considerations, the minimum radius of an ion around which other ions of unit radius can be arranged.

In a substance of the general formula CA , if the ratio of the cation radius to the anion radius, r_c/r_A , is less than 0.15, then only two anions can be arranged about a cation so that the three ions are in contact. Similarly, if the ratio is greater than 0.15, only three anions may be in contact with one cation at the same time. If the ratio is greater than 0.22, only four anions at tetrahedral corners can touch one cation.

For a ratio greater than 0.41 four anions may be arranged at the corners of a square, or six anions, at octahedral corners,

can be in contact with one cation. When the ratio is greater than 0.73, only eight anions, at the corners of a cube, may be in contact with one cation.

The first four postulated distributions of anions around a cation. The six hypothetical arrangements of ions within a crystal, calculated from radius-ratio rules, are given in table.

It has been customary to name each lattice type according to a familiar compound having that type of structure. For substances with the general formula CA the eightfold coordination is usually referred to as the *CsCl structure*, the sixfold coordination is called the *NaCl structure*, and the fourfold coordination is frequently denoted as the *zinc blende structure*, although this latter compound is itself covalent.

Of these three structures the first two are most common. In a crystal of the *NaCl* type each positive ion is surrounded by six negative ions arranged in an octahedron, and each negative ion is surrounded by six positive ions.

The packing of the ions in sodium chloride, and figure indicates the pattern in a unit cell of the sodium chloride structure.

A lattice is considered as being indefinite in extent and constructed of an infinite repetition of a small group of ions, the latter constituting an imaginary *unit cell*. This unit is the smallest portion of the crystal lattice which possesses all the various kinds of symmetry which characterize the crystal. Actually it is not possible for a single unit cell to exist alone, since the boundaries of the unit cell are also the boundaries of neighbouring unit cells.

The radii of sodium ions are less than the radii of chloride ions, and the sizes of the ions play a most important role in determining the lattice structure. Geometrically a crystal structure is as compact as the effective radii of the ions will permit, while at the same time keeping similar ions more or less separated by means of a region that is occupied by ions of opposite charge.

Table. Hypothetical Arrangements of Anions about a Cation as Calculated from Radius-ratio Rules

Coordination number Radius ratio, (number of anions) in crystal	Geometric arrangement	r_c/r_A
2	Linear	Up to 0.15
3	Triangular	0.15-0.22
4	Tetrahedral	0.22-0.41
4	Planar	0.41-0.73
6	Octahedral	0.41-0.73
8	Cubic	0.73 and
above		

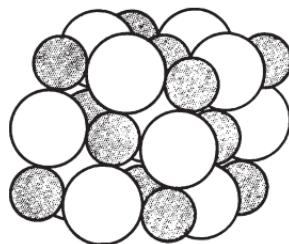


Fig. The Packing of the Ions in Sodium Chloride; the Small Spheres Represent Sodium Ions and the Large Spheres Chloride Ions

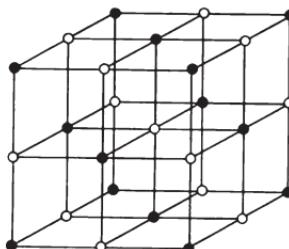
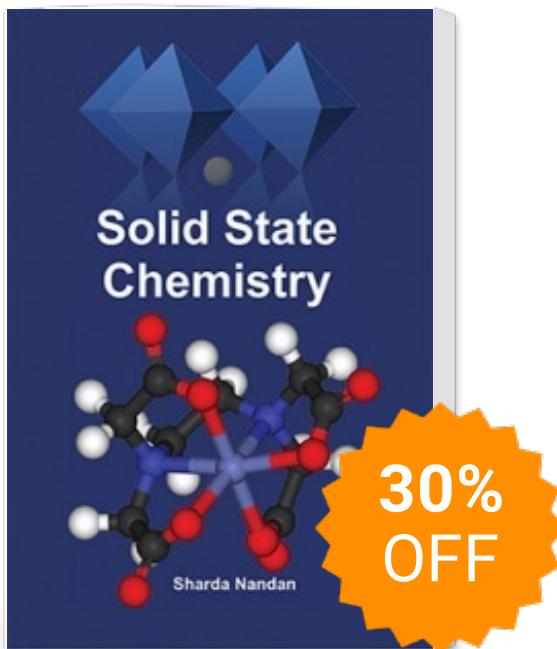


Fig. The Crystal Pattern of Sodium Chloride.

The sodium ions only, they are found to be located at the corners of a cube, with another sodium ion stationed in the centre of each of its faces. A crystal pattern of this type is known as the *face-centred cubic lattice*.

The ratio of the ionic radii in the sodium chloride lattice is approximately 0.53, and this value indicates that the radius of

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