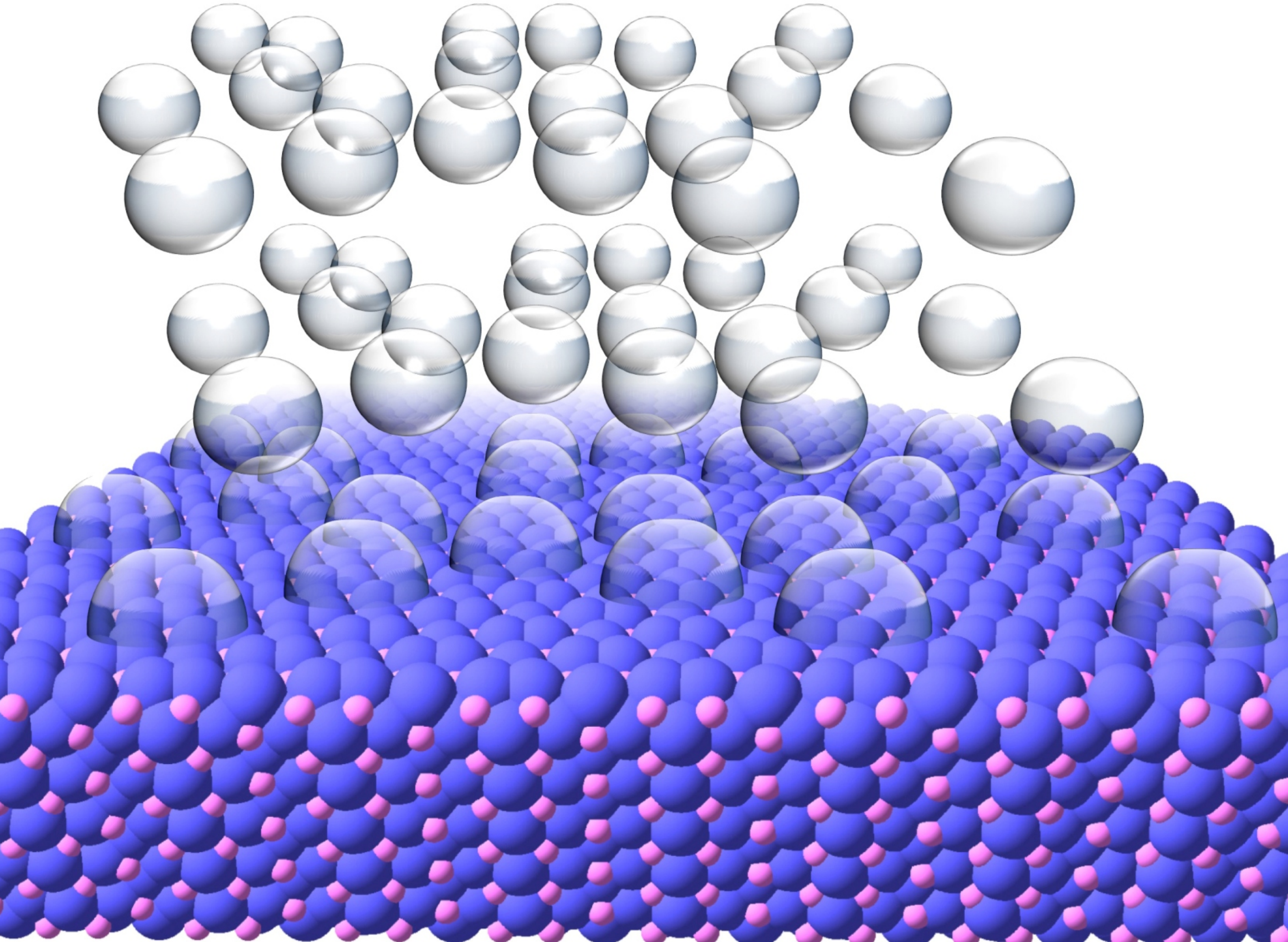
Crystal Structure in Solid State Chemistry

Corey Hunter



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CRYSTAL STRUCTURE

In mineralogy and crystallography, a crystal structure is a unique arrangement of atoms in a crystal. A crystal structure is composed of a motif, a set of atoms arranged in a particular way, and a lattice. Motifs are located upon the points of a lattice, which is an array of points repeating periodically in three dimensions. The points can be thought of as forming identical tiny boxes, called unit cells, that fill the space of the lattice. The lengths of the edges of a unit cell and the angles between them are called the lattice parameters. The symmetry properties of the crystal are embodied in its space group. A crystal's structure and symmetry play a role in determining many of its properties, such as cleavage, electronic band structure, and optical properties.

SOLIDS

Amorphous solids are homogeneous and isotropic because there is no long range order or periodicity in their internal atomic arrangement. By contrast, the crystalline state is characterised by a regular arrangement of atoms over large distances. Crystals are therefore anisotropic – their properties vary with direction. For example, the interatomic spacing varies with orientation within the crystal, as does the elastic response to an applied stress. Engineering materials are usually aggregates of many crystals of varying sizes and shapes; these polycrystalline materials have properties which depend on the nature of the individual crystals, but also on aggregate properties such as the size and shape distributions of the crystals, and the orientation relationships between the individual crystals. The randomness in the orientation of the crystals is a measure of texture, which has to be controlled in the manufacture of transformer steels, uranium fuel rods and beverage cans. The crystallography of interfaces connecting adjacent crystals can determine the deformation behaviour of the polycrystalline aggregate; it can also influence the toughness through its effect on the degree of segregation of impurities to such interfaces.

Metals and ceramics are the basic materials of nuclear reactors. The regular arrangement of the atoms in such solids is termed a crystal lattice. Pure solids (whether elemental or binary) need not retain the same crystal structure from low temperature to the melting point; iron and uranium exhibit three crystal structures, each confined to a definite temperature interval, but uranium dioxide has only one. The change from one crystal structure to another is called a phase transformation. Such changes are the solid-solid equivalents of melting and vaporization.

The crystal structure can exert a profound effect on material's behaviour in the environment of a nuclear reactor, as seen from the following examples:

- Void swelling can cause unacceptable dimensional changes in structures of fast reactors or fusion reactors (but not generally in light water reactors, except at higher doses and intermediate temperatures in austenitic stainless steels). The crystal structure of the austenitic form of steel is susceptible to this radiation effect but the different crystal structure of the ferritic form is immune until very high doses (>H"50 displacements per atom, dpa).
- Under fast-neutron irradiation, Zircaloy cladding of LWRs undergoes growth in the axial direction. This effect is due to the anisotropy of the crystal structure of zirconium.
- The relation between crystal anisotropy and the directional dependence of macroscopic properties in zirconium was covered in Sect I.2.

- The utility of uranium metal as a nuclear fuel is diminished because of the volume change accompanying a solid phase transformation that occurs at relatively low temperature.Imperfections in the crystal lattice are even more important than the details of the atomic structure.
- Missing atoms in the atomic lattice called vacancies, or extra atoms in nonregular positions called interstitials, are responsible for the mobility of atoms in the solid
- Many of the mechanical properties of metals are governed by a linear defect in the atomic structure called a dislocation
- All structural alloys and ceramic fuels consist of a large number of small crystals, or grains, joined at their peripheries. The discontinuities in the crystal structure at these internal surfaces are called grain boundaries. Their presence influences a variety of mechanical and transport properties, including cracking in steel and fission gas movement in fuel.

For elemental solids, only 14 distinct structures, or spatial arrangements of atoms, are possible. Each crystal structure is characterized by a unit cell, which is a small group of atoms that contains the unique features of the particular lattice type. A macroscopic crystal is composed of large numbers of unit cells stacked together.

The elemental and binary solids important in LWRs are restricted to only a few of the 14 possible lattice types, mainly those with the highest degrees of symmetry and the tightest packing of atoms. With one exception, these unit cells are parallelepipeds (all angles 90o) with side lengths denoted by a, b, and c.

The exception is a structure whose unit cell is a hexagonal prism with only two characteristic dimensions. Only the parallelepiped with all sides of equal length (*i.e.*, a cube) is isotropic. All the others are anisotropic, meaning that properties differ in the principal coordinate directions.

THE LATTICE

Crystals have translational symmetry: it is possible to identify a regular set of points, known as the lattice points, each of which has an identical environment. The set of these lattice points constitutes a three dimensional lattice. A unit cell may be defined within this lattice as a space–filling parallelepiped with origin at a lattice point, and with its edges defined by three non-coplanar basis vectors a1, a2 and a3, each of which represents translations between two lattice points. The entire lattice can then be generated by stacking unit cells in three dimensions. Any vector representing a translation between lattice points is called a lattice vector.

The unit cell defined above has lattice points located at its corners. Since these are shared with seven other unit cells, and since each cell has eight corners, there is only one lattice point per unit cell. Such a unit cell is primitive and has the lattice symbol P. Non–primitive unit cells can have two or more lattice points, in which case, the additional lattice points will be located at positions other than the corners of the cell. A cell with lattice points located at the centres of all its faces has the lattice symbol F; such a cell would contain four lattice points. Not all the faces of the cell need to have face–centering lattice points; when a cell containing two lattice points has the additional lattice point located at the centre of the face defined by a2 and a3, the lattice symbol is A and the cell is said to be A-centred. B-centred and C-centred cells have the additional lattice point located on the face defined by a3 & a1 or a1 & a2 respectively.

A unit cell with two lattice points can alternatively have the additional lattice point at the body-centre of the cell, in which case the lattice symbol is I. The lattice symbol R is for a trigonal cell; the cell is usually defined such that it contains three lattice points. The basis vectors a1, a2 and a3 define the the unit cell; their magnitudes a1, a2 and a3 respectively, are the lattice parameters of the unit cell. The angles a1^a2, a2^a3 and a3 ^a1 are conventionally labelled g,aand b respectively. Note that our initial choice of the basis vectors was arbitrary since there are an infinite number of lattice vectors which could have been used in defining the unit cell. The preferred choice includes small basis vectors which are as equal as possible, provided the shape of the cell reflects the essential symmetry of the lattice.

The Bravais Lattices

The number of ways in which points can be arranged regularly in three dimensions, such that the stacking of unit cells fills space, is not limitless; Bravais showed in 1848 that all possible arrangements can be represented by just fourteen lattices. The fourteen Bravais lattices can be categorised into seven crystal systems (cubic, tetragonal, orthorhombic, trigonal, hexagonal, monoclinic and triclinic); the cubic system contains for example, the cubic-P, cubic-F and cubic-I lattices. Each crystal system can be characterised uniquely by a set of defining symmetry elements, which any crystal within that system must possess as a minimum requirement.

The Bravais lattices are each as a projection along the a_3 axis. Projections like these are useful as simple representations of three–dimensional objects. The coordinate of any point with respect to the a_3 axis is represented as a fraction of a_3 along the point of interest; points located at $0a3$ are unlabelled; translational symmetry requires that for each lattice point located at $0a_3$, there must exist another at $1a_3$.

PHYSICAL PROPERTIES

Defects or 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.

Crystal Symmetry and Physical 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 center 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 in.

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. 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.

X-RAY CRYSTALLOGRAPHY

X-ray crystallography is an extremely precise, but also difficult and expensive means of imaging the exact structure of a given molecule or macromolecule in a crystal lattice. Because a diverse set of materials produce crystals, including salts, metals, minerals, semiconductors, and various inorganic, organic, and biological molecules, x-ray crystallography is essential to many scientific fields. A crystal is any regularly repeating arrangement of unit cells which range in size from less than 100 atoms — small-molecule crystallography — to tens of thousands — macromolecular crystallography).

X-ray crystallography is famous for being the tool first used to discover the structure of DNA, but it was also used to determine the structure of diamond, table salt, penicillin, numerous proteins, and entire viruses. In all, over 400,000 structures have been described using x-ray crystallography. These can be found in the Cambridge Structure Database.To analyse a sample using x-ray crystallography, first one must obtain a high-purity crystal of the material to be studied with a very regular structure. This is often the hardest part as numerous crystals have nanometer-scale defects which make x-ray crystallography difficult.

Next, the sample is subjected to an intense beam of x-rays of a uniform wavelength. These x-rays produce a diffraction pattern as they reflect off the sample. This diffraction pattern is somewhat similar to what is observed when multiple stones are tossed into a pond – where the waves cross are peaks which make up the diffraction pattern. By slowly rotating the crystal, pounding it with x-rays, and meticulously recording the diffraction patterns at each orientation, an electron density map may be derived. This electron density map is then used to formulate a hypothesis about the atomic structure it corresponds to. The diffraction patterns are then analysed in light of the hypothesized structure, and if it looks plausible that the given structure would produce the observed diffraction pattern, a conclusion is drawn. The result is then uploaded to central databases of the type mentioned earlier.

X-RAYS AND THE PRODUCTION OF X-RAYS

X-rays are electromagnetic radiation with wavelengths between about 0.02 Å and 100 Å (1Å = 10-10 meters). They are part of the electromagnetic spectrum that includes wavelengths of electromagnetic radiation called visible light which our eyes are sensitive to (different wavelengths of visible light appear to us as different colours). Because X-rays have wavelengths similar to the size of atoms, they are useful to explore within crystals.

The energy of X-rays, like all electromagnetic radiation, is inversely proportional to their wavelength as given by the Einstein equation:

$$E = h = hc$$

where:

- E = energy
- h = Planck's constant, 6.62517 × 10-27 erg.sec = frequency
- c = velocity of light = 2.99793 × 1010 cm/sec = wavelength

Thus, since X-rays have a smaller wavelength than visible light, they have higher energy. With their higher energy, X-rays can penetrate matter more easily than can visible light. Their ability to penetrate matter depends on the density of the matter, and thus X-rays provide a powerful tool in medicine for mapping internal structures of the human body (bones have higher density than tissue, and thus are harder for X-rays to penetrate, fractures in bones have a different density than the bone). X-rays are produced in a device called an X-ray tube. Such a tube is illustrated here. It consists of an evacuated chamber with a tungsten filament at one end of the tube, called the cathode, and a metal target at the other end, called an anode. Electrical current is run through the tungsten filament, causing it to glow and emit electrons. A large voltage difference (measured in kilovolts) is placed between the cathode and the anode, causing the electrons to move at high velocity from the filament to the anode target. Upon striking the atoms in the target, the electrons dislodge inner shell electrons resulting in outer shell electrons having to jump to a lower energy shell to replace the dislodged electrons. These electronic transitions results in the generation of X-rays. The X-rays then move through a window in the X-ray tube and can be used to provide information on the internal arrangement of atoms in crystals or the structure of internal body parts.

CONTINUOUS AND CHARACTERISTIC X-RAY SPECTRA

When the target material of the X-ray tube is bombarded with electrons accelerated from the cathode filament, two types of X-ray spectra are produced. The first is called the continuous spectra. The continuous spectra consists of a range of wavelengths of X-rays with minimum wavelength and intensity (measured in counts per second) dependent on the target material and the voltage across the X-ray tube. The minimum wavelength decreases and the intensity increases as voltage increases.

The second type of spectra, called the characteristic spectra, is produced at high voltage as a result of specific electronic transitions that take place within individual atoms of the target material. This is easiest to see using the simple Bohr model of the atom. In such a model, the nucleus of the atom containing the protons and neutrons is surrounded by shells of electrons. The innermost shell, called the K- shell, is surrounded by the L- and M - shells. When the energy of the electrons accelerated towards the target becomes high enough to dislodge K- shell electrons, electrons from the L -

and M - shells move in to take the place of those dislodged. Each of these electronic transitions produces an X-ray with a wavelength that depends on the exact structure of the atom being bombarded. A transition from the L - shell to the K-shell produces a K X-ray, while the transition from an M - shell to the K- shell produces a K X-ray.

These characteristic X-rays have a much higher intensity than those produced by the continuous sprectra, with K X-rays having higher intensity than K X-rays. The important point here is that the wavelength of these characteristic x-rays is different for each atom in the periodic table (of course only those elements with higher atomic number have L– and M– shell electrons that can undergo transitions to produce X-rays). A filter is generally used to filter out the lower intensity K X-rays.

For commonly used target materials in X-ray tubes, the X-rays have the following well-known experimentally determined wavelengths:

Element	**K Wavelength () Å**
Mo	0.7107
Cu	1.5418
Co	1.7902
Fe	1.9373
Cr	2.2909

X-RAY DIFFRACTION AND BRAGG'S LAW

Since a beam of X-rays consists of a bundle of separate waves, the waves can interact with one another. Such interaction is termed interference. If all the waves in the bundle are in phase, that is their crests and troughs occur at exactly the same position (the same as being an integer number of wavelengths out of phase, $n = 1, 2, 3, 4$, etc.), the waves will interfere with one another and their amplitudes will add together to produce a resultant wave that is has a higher amplitude (the sum of all the waves that are in phase.

If the waves are out of phase, being off by a non-integer number of wavelengths, then destructive interference will occur and the amplitude of the waves will be reduced. In an extreme case, if the waves are out of phase by a multiple of 1/2 ($n/2$), the resultant wave will have no amplitude and thus be completely destroyed. The atoms in crystals interact with X-ray waves in such a way as to produce interference. The interaction can be thought of as if the atoms in a crystal structure reflect the waves. But, because a crystal structure consists of an orderly arrangement of atoms, the reflections occur from what appears to be planes of atoms.

Let's imagine a beam of X-rays entering a crystal with one of these planes of atoms oriented at an angle of to the incoming beam of monochromatic X-rays (monochromatic means one colour, or in this case 1 discreet wavelength as produced by the characteristic spectra of the X-ray tube). Two such X-rays are shown here, where the spacing between the atomic planes occurs over the distance, d. Ray 1 reflects off of the upper atomic plane at an angle ? equal to its angle of incidence. Similarly, Ray 2 reflects off the lower atomic plane at the same angle. While Ray 2 is in the crystal, however, it travels a distance of 2a farther than Ray 1. If this distance 2a is equal to an integral number of wavelengths (n?), then Rays 1 and 2 will be in phase on their exit from the crystal and constructive interference will occur. If the distance 2a is not an integral number of wavelengths, then destructive interference will occur and the waves will not be as strong as when they entered the crystal. Thus, the condition for constructive interference to occur is,

$$n = 2a$$

but, from trigonometry, we can figure out what the distance 2a is in terms of the spacing, d, between the atomic planes.

$a = d \sin$

or $2a = 2d \sin$

thus, $n = 2d \sin$

This is known as Bragg's Law for X-ray diffraction.

What it says is that if we know the wavelength ,? , of the X-rays going in to the crystal, and we can measure the angle ? of the diffracted X-rays coming out of the crystal, then we know the spacing (referred to as d-spacing) between the atomic planes.

$$d = \frac{n}{2 \sin}$$

Again it is important to point out that this diffraction will only occur if the rays are in phase when they emerge, and this will only occur at the appropriate value of n (1, 2, 3, etc.) and?. In theory, then we could re-orient the crystal so that another atomic plane is exposed and measure the d-spacing between all atomic planes in the crystal, eventually leading us to determine the crystal structure and the size of the unit cell.

THE X-RAY POWDER METHOD

In practice, this would be a time consuming operation to reorient the crystal, measure the angle ?, and determine the d-spacing for all atomic planes. A faster way is to use a method called the powder method. In this method, a mineral is ground up to a fine powder. In the powder, are thousands of grains that have random orientations. With random orientations we might expect most of the different atomic planes to lie parallel to the surface in some of the grains. Thus, by scanning through an angle ??of incident X-ray beams form 0 to 90o, we would expect to find all angles where diffraction has occurred, and each of these angles would be associated with a different atomic spacing.

The instrument used to do this is an x-ray powder diffractometer. It consists of an X-ray tube capable of producing a beam of monochromatic X-rays that can be rotated to produce angles from 0 to 90°. A powdered mineral sample is placed on a sample stage so that it can be irradiated by the X-ray tube. To detect the diffracted X-rays, an electronic detector is placed on the other side of the sample from the X-ray tube, and it too is allowed to rotate to produce angles from 0 to 90°.

The instrument used to rotate both the X-ray tube and the detector is called a goniometer. The goniometer keeps track of the angle and sends this information to a computer, while the detector records the rate of X-rays coming out the other side of the sample (in units of counts/sec) and sends this information to the computer.

After a scan of the sample the X-ray intensity can be plotted against the angle (usually reported as 2 because of the way older diffractometers were made) to produce a chart, like the one shown here. The angle 2 for each diffraction peak can then be converted to d-spacing, using the Bragg equation.

One can then work out the crystal structure and associate each of the diffraction peaks with a different atomic plane in terms of the Miller Index for that plane (hkl). A group known as the Joint Committee on Powder Diffraction Standards (JCPDS) has collected data such as this on thousands of crystalline substances.

This data can be obtained as the JCPDS Powder Diffraction File. Since every compound with the same crystal structure will produce an identical powder diffraction pattern, the pattern serves as kind of a “fingerprint” for the substance, and thus comparing an unknown mineral to those in the Powder Diffraction file enables easy identification of the unknown.

CRYSTALS AND X-RAYS

Crystals have long been admired for their regularity and symmetry, but they were not investigated scientifically until the 17th century. Johannes Kepler hypothesized in his work Strena seu de Nive Sexangula that the hexagonal symmetry of snowflake crystals was due to a regular packing of spherical water particles. As shown by X-ray crystallography, the hexagonal symmetry of snowflakes results from the tetrahedral arrangement of hydrogen bonds about each water molecule. The water molecules are arranged simiarly to the silicon atoms in the tridymite polymorph of SiO_2. The resulting crystal structure has hexagonal symmetry when viewed along a principal axis.

Crystal symmetry was first investigated experimentally by Nicolas Steno who showed that the angles between the faces are the same in every exemplar of a particular type of crystal who discovered that every face of a crystal can be described by simple stacking patterns of blocks of the same shape and size. Hence, William Hallowes Miller in 1839 was able to give each face a unique label of three small integers, the Miller indices which are still used today for identifying crystal faces. Haüy's study led to the correct idea that crystals are a regular three-dimensional array (a Bravais lattice) of atoms and molecules; a single unit cell is repeated indefinitely along three principal directions that are not necessarily perpendicular. In the 19th century, a complete catalog of the possible symmetries of a crystal was worked out by Johann Hessel, Auguste Bravais, Yevgraf Fyodorov,, Arthur Schφnflies and (belatedly) William Barlow. On the basis of the available data and physical reasoning, Barlow proposed several crystal structures in the 1880s that were validated later by X-ray crystallography; however, the available data were too few in the 1880s to accept his models as conclusive.

X-rays were discovered by Wilhelm Conrad Rφntgen in 1895, just as the studies of crystal symmetry were being concluded. Physicists were initially uncertain of the nature of X-rays, although it was soon suspected (correctly) that they were waves of electromagnetic radiation, in other words, another form of light. At that time, the wave model of light — specifically, the Maxwell theory of electromagnetic radiation — was well accepted among scientists, and experiments by Charles Glover Barkla showed that X-rays exhibited phenomena associated with electromagnetic waves, including transverse polarization and spectral lines akin to those observed in the visible wavelengths. Single-slit experiments in the laboratory of Arnold Sommerfeld suggested the wavelength of X-rays was roughly 1 Angstrφm, one ten millionth of a millimetre.

However, X-rays are composed of photons, and thus are not only waves of electromagnetic radiation but also exhibit particle-like properties. The photon concept was introduced by Albert Einstein in 1905, but it was not broadly accepted until 1922, when Arthur Compton confirmed it by the scattering of X-rays from electrons. Therefore, these particle-like properties of X-rays, such as their ionization of gases, caused William Henry Bragg to argue in 1907 that X-rays were not electromagnetic radiation. Nevertheless, Bragg's view was not broadly accepted and the observation of X-ray diffraction in 1912 confirmed for most scientists that X-rays were a form of electromagnetic radiation.

X-rays Analysis of Crystals

The incoming beam (coming from upper left) causes each scatterer to re-radiate a small portion of its energy as a spherical wave. If scatterers are arranged symmetrically with a separation d, these spherical waves will be in synch (add constructively) only in directions where their path-length difference 2d sin θ equals an integer multiple of the wavelength λ. In that case, part of the incoming beam is deflected by an angle 2θ, producing a reflection spot in the diffraction pattern.

Crystals are regular arrays of atoms, and X-rays can be considered waves of electromagnetic radiation. Atoms scatter X-ray waves, primarily through the atoms' electrons. Just as an ocean wave striking a lighthouse produces secondary circular waves emanating from the lighthouse, so an X-ray striking an electron produces secondary spherical waves emanating from the electron. This phenomenon is known as scattering, and the electron (or lighthouse) is known as the scatterer. A regular array of scatterers produces a regular array of spherical waves. Although these waves cancel one another out in most directions (destructive interference), they add constructively in a few specific directions, determined by Bragg's law,

$$2d \sin \theta = n\lambda$$

where n is any integer. These specific directions appear as spots on the diffraction pattern, often called reflections. Thus, X-ray diffraction results from an electromagnetic wave (the X-ray) impinging on a regular array of scatterers (the repeating arrangement of atoms within the crystal).

X-rays are used to produce the diffraction pattern because their wavelength λ is typically the same order of magnitude (1-100 Ångstrφms) as the spacing d between planes in the crystal. In principle, any wave impinging on a regular array of scatterers produces diffraction, as predicted first by Francesco Maria Grimaldi in 1665. To produce significant diffraction, the spacing between the scatterers and the wavelength of the impinging wave should be roughly similar in size. For illustration, the diffraction of sunlight through a bird's feather was first reported by James Gregory in the later 17th century. The first man-made diffraction gratings for visible light were constructed by David Rittenhouse in 1787, and Joseph von Fraunhofer in 1821. However, visible light has too long a wavelength (typically, 5500 Ångstrφms) to observe diffraction from crystals. However, prior to the first X-ray diffraction experiments, the spacings between lattice planes in a crystal were not known with certainty.

The idea that crystals could be used as a diffraction grating for X-rays arose in 1912 in a conversation between Paul Peter Ewald and Max von Laue in the English Garden in Munich. Ewald had proposed a resonator model of crystals for his thesis, but this model could not be validated using visible light, since the wavelength was much larger than the spacing between the resonators. Von Laue realised that electromagnetic radiation of a shorter wavelength was needed to observe such small spacings, and suggested that X-rays might have a wavelength comparable to the unit-cell spacing in crystals. Von Laue worked with two technicians, Walter Friedrich and his assistant Paul Knipping, to shine a beam of X-rays through a sphalerite crystal and record its diffraction on a photographic plate. After being developed, the plate showed a large number of well-defined spots arranged in a pattern of intersecting circles around the spot produced by the central beam. Von Laue developed a law that connects the scattering angles and the size and orientation of the unit-cell spacings in the crystal, for which he was awarded the Nobel Prize in Physics in 1914.

As described in the mathematical derivation below, the X-ray scattering is determined by the density of electrons within the crystal. Since the energy of an X-ray is much greater than that of an atomic electron, the scattering may be modeled as Thomson scattering, the interaction of an electromagnetic ray with a free electron. This model is generally adopted to describe the polarization of the scattered radiation. The intensity of Thomson scattering declines as $1/m^2$ with the mass m of the charged particle that is scattering the radiation; hence, the atomic nuclei, which are thousands of times heavier than an electron, contribute negligibly to the scattered X-rays.

GENERATION OF X-RAYS

RONTGEN'S DISCOVERY

X-Rays were discovered by Wilhelm Rφntgen in 1895, for which he was awarded the first Nobel Prize in Physics in 1901. The original records of Rφntgen's experiments were lost, but a reconstruction of them in Moore and Reynolds is very interesting. Basically, he discovered that in an experiment with high-energy electrons, another type of radiation was being produced which had the following unique properties:

- Travels in straight lines
- Are exponentially absorbed in matter with the exponent proportional to the mass of the absorbing material
- Darkens photographic plates
- Make shadows of absorbing material on photosensitive paper

The 4th property led directly to the use of x-rays in medicine. In the years following Rφntgen's discovery, much was learned about x-rays, and much of the wave vs. particle arguments about radiation which consumed science in the early part of the 20th century were rooted in studies of x-rays.

DISCOVERY OF DIFFRACTION

Studies of x-rays revealed that they could be polarized, but could not be refracted, leading to controversy over whether x-rays were particles or waves. It was understood that if they were waves, the wavelength must be extremely small (10-10 meters or less). Max von Laue theorized that if x-rays could also be diffracted if the slits were small enough. Since it was understood that molecular spacings in crystalline materials were on the order of a tenth of a nanometer, he devised an experiment in which x-rays were allowed into a lead box containing a crystal, with sensitive film behind the crystal.

When the films were developed there was a large central point from the incident x-rays, but also many smaller points in a regular pattern. These could only be due to the diffraction of the incident beam and the interference of many beams. By using a crystal as a diffraction grating, von Laue had proved the x-rays were not particles, but waves of light with very small wavelengths. He published his results in 1912.

Lawrence Bragg and his father W.H. Bragg used von Laue's discovery and, for monochromatic radiation, were able to show that diffraction could be treated geometrically like reflection.

They derived Bragg's law, which allows diffraction to be treated in simple mathematical terms.

The Bragg equation provides a simplified framework for diffraction that works for basic calculations:

$$n\lambda = 2d \sin \theta,$$

Where,

n is an integer

λ is the wavelength of the X-radiation

d is the interplanar spacing in the crystalline material and

θ is the diffraction angle

GENERATION OF X-RAYS

Much of this section is abstracted from Jenkins and Snyder with parts from Moore and Reynolds, X-rays are short-wavelength, high-energy electromagnetic radiation, having the properties of both waves and particles.

They can be described in terms of both photon energy (E) or wavelength, λ (lamda – the distance between peaks) and frequency ν (nu – the number of peaks passing a point in a unit of time). The relationships between these quantities are expressed in the following equations:

$$\upsilon = \frac{c}{\lambda}$$

and $E = h\upsilon$

where E is the energy of the electron flux in *KeV*

h is Planck's constant (4.135 × 10-15 *eVs*)

c is the speed of light (3 × 1018 Å/*s*)

λ is the wavelength in Å

Substituting the first equation in the second yields:

$$E = \frac{hc}{\lambda}$$

which describes the energy of x-rays in terms of their wavelength. Substituting the values of the constants above in the equation yields the following relationship:

$$E = \frac{12.398}{\lambda}$$

Immediately apparent from this equation is that there is an inverse relationship between the energy and wavelength of x-rays.

Continuous Radiation

X-rays are produced whenever matter is irradiated with a beam of high-energy charged particles or photons. Interactions that occur between the beam (*i.e.*, electrons) and target will result in a loss of energy. Since energy must be conserved, the energy loss results in the release of x-ray photons of energy (wavelength) equal to the energy loss, This process generates a broad band of continuous radiation (a.k.a. bremsstrahlung or white radiation). This (along with the higher-intensity characteristic lines) (for a Cu target at a variety of kV) as the low-intensity spectrum.

Note that for any given accelerating potential (8.5, 25 and 50 *kV*), there is a minimum wavelength of x-rays generated. The minimum wavelength at which the continuum begins is related to the maximum accelerating potential of the beam of electrons directed at the target, V, by the following equation,

$$l \text{ min} = \frac{hc}{V} = \frac{12.398}{V},$$

Note from the shape of the curve that the continuum reaches a maximum intensity at a wavelength of about 1.5 to 2 times the λmin. The sharp peaks labeled as characteristic lines on the diagram are not present at the continuum at 8.5 *kV*, but are present in the curve at 25 *kV*. The characteristic lines only will appear when the critical excitation potential for the anode in use is exceeded.

CHARACTERISTIC RADIATION (AND "FILTERING")

Successful analysis of powders by x-ray diffraction requires the Bragg diffraction condition to be met, which, in turn, requires high-intensity monochromatic radiation. In the standard powder diffractometer, this radiation is obtained by the generation of very high-intensity "characteristic" x-rays of known wavelength with an x-ray tube. The characteristic radiation (which consists of several wavelengths) along with the continuous spectrum is then "filtered" by means of an absorptive filter, a crystal monochromator, a wavelength-selective detector or a combination of these devices. Both of the generation of characteristic x-rays and the filtering processes will be addressed in this section.

GENERATION OF CHARACTERISTIC X-RAYS

The simplified discussion below uses Cu as an example. The same process applies to all of the anodes listed in Table 1 above. The quantum physics related to the generation of x-rays is, in reality, much more complicated, but this simplified discussion works for our purposes. If a high-energy electron or photon interacts with electrons in the target anode atoms such that an inner orbital electron is displaced, an electron from a lower energy shell will "jump" to replace the displaced higher-energy electron. This results in the generation of an x-ray photon of quantum energy equal to that of the transition. The relationship between the energy of this x-ray and its wavelength is described by equation.

If an Lshell electron moves to replace it, a Kα x-ray is produced. If an M-shell electron moves to replace it, a Kβ x-ray is produced. The selection rules of quantum transitions in the atom indicate what transitions will occur. These transitions are shown diagrammatically in the figure below. Two discrete energy "shifts" occur in the L- to K-shell levels transition, yielding Kα1 (8.045 keV, 1.5406Å) and Kα2 (8.025 keV, 1.5444Å) x-rays. The intensity of the resultant x-rays is related to the number of times the particular transition occurs. The Kα1 transition will occur almost exactly twice as frequently as the Kα2 transition, thus the resultant x-rays have twice the intensity. Although three M to K transitions can occur in Cu, the energy difference between two of them is so small that Kβ1 and Kβ2 (8.903 keV, 1.3922Å) x-rays are effectively monochromatic, and the intensity of the Kβ5 transition is low enough to be ignored. In the diagram below the energies of the various possible energy transitions are shown at left, and the resultant characteristic x-ray spectrum at right. It is important to be clear about the distinction between wavelength (energy) and intensity. Since the Kβ (M'!K) transition involves a larger energy transition, the resultant x-rays have higher energy (lower wavelength) than the Kα (L'!K) x-rays. Kα transition, however, occurs much more frequently, thus the resultant x-rays have a much higher intensity. Spectrum for a Cuanode x-ray tube at a variety of accelerating voltages. Note how much the intensity of the Kα and Kβ x-rays exceed that of the continuum at 25 keV, and that at 50 keV the Kα1 peak is way off the top of the intensity scale. Each of the common anode elements will tend to have an optimum operating voltage in which the intensity of the characteristic Kα radiation will greatly exceed that of the continuum; these optimum values are listed for the common anode materials. The x-ray tube will produce several different characteristic-energy radiations plus the continuum.

MAKING MONOCHROMATIC X-RAYS

There are a number of ways that x-rays "out of the tube" can be modified such that the radiation detected after diffraction is only Kα.

Some of these methods include:

- Use of a β filter
- Use of proportional detector and pulse height selection
- Use of a Si(Li) solid-state detector
- Use of a diffracted- or primary-beam monochromator

These methods will be discussed briefly below. Most texts discuss these methods. The treatment by Ron Jenkins in Bish and Post is very concise. The material in this section is abstracted from both sources. Though the x-ray spectrum is more complicated, we are mostly concerned with the strong characteristic lines generated by our x-ray source. These lines are listed below for the common anodes:

Table: Characterisitic Wavelength Values (in Å) for Common Anode Materials

Anode	**Kα_1(100)**	**Kα_2(50)**	**Kβ(15)**
Cu	1.54060	1.54439	1.39222
Cr	2.28970	2.29361	2.08487
Fe	1.93604	1.93998	1.75661
Co	1.78897	1.79285	1.62079
Mo	0.70930	0.71359	0.63229

There is no effective way to remove the Kα2 peak from the incident or diffracted beam. At low angles in the diffractogram, the Kα1 – Kα2 doublet is poorly resolved and will be reflected as a slight asymmetry of the diffraction peak. At higher angles, the doublet will be resolved into two discrete peaks as the angular dispersion of the doublet increases. The known angular dispersion of the doublet and the intensity relationship (the α2 peak is always about ½ the intensity of the α2 peak) is used in analytical software to digitally filter the Kα2 peak from the resultant diffractogram.

β Filters (and Detector "Tuning")

Filtration is a process by which undesirable characteristic radiation is preferentially absorbed by a filtering material while most of the desired characteristic radiation is passed. Absorption and absorption edges are discussed extensively in Jenkins and Snyder from which most of this discussion is abstracted. All materials absorb x-rays, and several processes operate to produce the mass absorption response of a given material to x-rays. One type of absorption is fundamentally linear and dependent primarily to electron density (mass) of the absorber. Another type is photoelectric absorption, which is related to secondary excitation of orbital electrons in the absorber.

This type of absorption is non-linear and varies significantly depending on the wavelength of the x-rays; the point in the wavelength spectrum to which absorption rises gradually and then drops abruptly is called an absorption edge. By selection of a an element for a filter whose absorption edge lies between the characteristic Kβ and Kα wavelength, the Kβ radiation can be greatly attenuated while most of the Kα radiation is passed. A Ni filter is used to filter Cu radiation. Below is the x-ray spectrum for a Copper target xray source overlain by the absorption curve for Ni. When used as a filter, the resultant intensity of the transmitted Cu radiation will be the Cu spectrum minus the Ni absorption curve. The table lists the common anode (target) elements and their β-filtering elements. It is common practice in the industry to choose a filter thickness that yields a Kα:Kβ intensity ratio between 50:1 and 25:1.

Target	**Ka(A)**	**β-filter**	**Thickness (μm)**	**(g/cc)**	**Bensity passed**	**% Kα passed**	**% Kβ**
	Cr	2.291	V	11	6.00	58	3
	Fe	1.937	Mn	11	7.43	59	3
	Co	1.791	Fe	12	7.87	57	3
	Cu	1.542	Ni	15	8.90	52	2
Mo	0.710	Zr	81	6.50	44	1	

With a diffractometer, if a filter is used, may be placed on the tube or detector side of the specimen, though the tube-side placement tends to be more common. For Debye-Scherrer powder cameras the filter will be between the source and the camera. As will be noted from the diagram above, while the Kβ radiation is very effectively filtered, a significant amount of the high-energy portion of the continuous spectrum will be passed. In film work this can be a problem and lead to significant fogging of the film; this is one reason that generators used for powder camera work are commonly operated at lower than "optimum" accelerating voltages (*i.e.*, 25 or 30 kV instead of 40 or 45 kV). In the powder diffractometer, pulse height discrimination in the detector electronics can be used to limit the energy of x-rays seen (*i.e.*, detected) by the detector, effectively removing the high-energy continuum and radiation produced by sample fluorescence.

This method is used on our Scintag PAD V diffractometer in combination with a detector-side monochromator. Some detector types of detectors (most commonly Si(Li) detectors1) allow very fine frequency discrimination or tuning such that it only "sees" a particular wavelength, usually only Kα. This eliminates the need for filters or monochromators and produces data with very high peak intensity and reduced background. The ability to tune the detector to a particular wavelength also allows the use of lower intensity but spectrally simpler Kβ radiation in experiments. Si(Li) detectors are in widespread use in large high-production industrial and commercial laboratories. Their disadvantages lie in their initial higher expense, requirements for special cooling while operating and higher dead time in relation to scintillation counters. The advantages and disadvantages of different types of detectors will be discussed later in this course.

Monochromators

The most common way x-rays are filtered on diffractometers, particularly those using scintillation detectors, is by use of a monochomator in either the primary or diffracted beam. These devices make use of the fact that each component wavelength of a polychromatic beam of radiation directed at a single crystal of known orientation and d-spacing will be diffracted at a discrete angle (following the Bragg law). By choosing a crystal with the dspacing to focus only the desired radiation (usually Kα), undesired radiation of all other wavelengths is dispersed and does not enter the detector. Whereas a filter selectively attenuates Kβ, a monochromator selectively passes the desired wavelength and attenuates everything else.

High-level bremsstrahlung and other errant radiation from anode contamination (except that in the energy "band" passed by the monochromator) will not get to the detector. This allows the operation of the x-ray generator optimal accelerating voltages without significantly increasing background "noise" in the detected signal.

Possible geometric configurations of monochromators in the beam path are shown in the diagram below and include:

- Diffracted beam parallel,
- Diffracted beam antiparallel,
- Primary beam. In general the diffracted beam parallel configuration is most common; it passes a strong characteristic signal because of minimal path from monochromator to detector, and will remove radiation due to sample fluorescence.

A planar crystal used in a monochromator will tend to diffract the selected wavelength over a very narrow range of incident angles, and will not be very effective in delivering a strong signal to the detector. For this reason, precisely deformed and machined synthetic curved crystals were developed. The pyrolitic graphite curved crystal monochromator is the most widely used crystal monochromator in use. By varying the position of the crystal and the receiving slits within the monochromator assembly, the wavelength passed may be modified. In general, to maximize intensity of the diffracted signal, it is set to pass all Kα radiation, and to not pass Kβ radiation. Our Scintag PAD V system has a diffracted beam parallel monochromator utilizing a synthetic curved graphite crystal. The photograph below shows the receiving slits, monochromator and scintillation detector. Note that the monochromator radius is equal to the distance between the receiving slit (closest to the detector) and the center of the monochromator, and between the center of the monochr-omator and the detector.

X-RAY DIFFRACTION AND SCANNING PROBE MICROSCOPY

X-Ray Diffraction

Diffraction can occur when electromagnetic radiation interacts with a periodic structure whose repeat distance is about the same as the wavelength of the radiation. Visible light, for example, can be diffracted by a grating that contains scribed lines spaced only a few thousand angstroms apart, about the wavelength of visible light. X-rays have wavelengths on the order of angstroms, in the range of typical interatomic distances in crystalline solids. Therefore, X-rays can be diffracted from the repeating patterns of atoms that are characteristic of crystalline materials.

Electromagnetic Properties of X-Rays

The role of X-rays in diffraction experiments is based on the electromagnetic properties of this form of radiation. Electromagnetic radiation such as visible light and X-rays can sometimes behave as if the radiation were a beam of particles, while at other times it behaves as if it were a wave. If the energy emitted in the form of photons has a wavelength between 10-6 to 10-10 cm, then the energy is referred to as X-rays. Electromagnetic radiation can be regarded as a wave moving at the speed of light, c (~3 x 1010 cm/s in a vacuum), and having associated with it a wavelength, ?, and a frequency, ?, such that the relationship c = ???is satisfied.

X-Rays and Crystalline Solids

In 1912, Maxwell von Laue recognized that X-rays would be scattered by atoms in a crystalline solid if there is a similarity in spatial scales. If the wavelength and the interatomic distances are roughly the same, diffraction patterns, which reveal the repeating atomic structure, can be formed. A pattern of scattered X-rays (the diffraction pattern) is mathematically related to the structural arrangement of atoms causing the scattering.

When certain geometric requirements are met, X-rays scattered from a crystalline solid can constructively interfere, producing a diffracted beam. Sir Lawrence Bragg simulated the experiment, using visible light with wavelengths thousands of times larger than those of X-rays. He used tiny arrays of dots and pinholes to mimic atomic arrangements on a much larger scale. Optical transform experiments, in which visible light is diffracted from arrays, yield diffraction patterns similar to those produced by shining X-rays on crystalline solids. However, the optical transform experiment is easier and safer than X-ray experiments and can be used in the classroom.

How Diffraction Patterns are Made

When electromagnetic radiation from several sources overlaps in space simultaneously, either constructive or destructive interference occurs. Constructive interference occurs when the waves are moving in step with one another. The waves reinforce one another and are said to be in phase. Destructive interference, on the other hand, occurs when the waves are out of phase, with one wave at a maximum amplitude, while the other is at a minimum amplitude. Interference occurs among the waves scattered by the atoms when crystalline solids are exposed to X-rays. The atoms in the crystal scatter the incoming radiation, resulting in diffraction patterns. Destructive interference occurs most often, but in specific directions constructive interference occurs.

Purpose of X-Ray Diffraction

Diffraction data has historically provided information regarding the structures of crystalline solids. Such data can be used to determine molecular structures, ranging from simple to complex, since the relative atomic positions of atoms can be determined. X-ray diffraction provided important evidence and indirect proof of atoms. Diffraction patterns constitute evidence for the periodically repeating arrangement of atoms in crystals. The symmetry of the diffraction patterns corresponds to the symmetry of the atomic packing. X-ray radiation directed at the solid provides the simplest way to determine the interatomic spacing that exists. The intensity of the diffracted beams also depends on the arrangement and atomic number of the atoms in the repeating motif, called the unit cell. Thus, the intensities of diffracted spots calculated for trial atomic positions can be compared with the experimental diffraction intensities to obtain the positions of the atoms themselves.

From this as well as other indirect methods such as stoichiometric relationships and thermodynamics, evidence of atoms was obtained. However, a direct way to image atoms on the surfaces of materials now exists. Developed in the mid-1980's, the scanning tunneling microscope (STM) permits direct imaging of atoms.

Scanning Probe Microscopy (SPM)

Scanning Probe Microscopy (SPM) includes Scanning Tunneling Microscopy (STM), Atomic Force Microscopy (AFM), and a variety of related experimental techniques. These are experimental methods that are used to image both organic and inorganic surfaces with (near) atomic resolution. In a scanning tunneling microscope a sharp metal tip, terminating ideally in a single atom, is positioned over an electrically conducting substrate, and a small potential difference is applied between them. The gap between the tip and the substrate surface is made large enough that electrical conduction cannot occur; yet, it is small enough to let electrons tunnel (a quantum mechanical phenomenon) between the tip and the surface. Tunneling probability decays exponentially with increasing tip-to-surface separation. Thus, the spatial arrangement of atoms on the surface is determined by the variation in tunneling current sensed by the probe tip as it moves in atomic-scale increments across the surface, a process called rastering. Scanning is more commonly done by adjusting the tip-to-surface separation so as to maintain a constant tunneling current, thereby preventing the tip from crashing into the surface. In either mode of operation a "map" of the sample surface with atomic resolution results.

Atomic Force Microscopy (AFM)

In an atomic force microscope the surface topography is mapped by measuring the mechanical force between tip and surface rather than the electrical current flowing between them as the STM does. Since force is used to create the images rather than the electrical current, the AFM can be used to image both conducting and non-conducting substrates. To measure the interatomic force, the tip of the AFM is mounted on the end of a small cantilever. As the interatomic force varies, the deflection of the lever can be sensed by bouncing a laser beam off the back of the lever and measuring displacements with a pair of photosensors.

Electrons and the Scanning Tunneling Microscope (STM)

Gert Binnig and Heinrich Rohrer were awarded the Nobel Prize in Physics, in 1986, for the development of the scanning tunneling microscope. They were also jointly honoured with Ernst Ruska for their work on the development of electron microscopy.

To gain a better understanding of how the scanning tunneling microscope works, the behaviour of electrons in metals and other electrically conducting material needs to be considered. Electrostatic forces acting between the electrons and the nuclei of atoms hold the atoms of a metal together. Core electrons are bound tightly to individual nuclei. However, the valence electrons that are farthest from the nuclei feel a relatively weak electrostatic attraction and are free to move about in the space between the nuclei. Since these electrons carry or conduct the electric current, they are referred to as conduction electrons. The large numbers of valence electron orbitals overlap and provide a continuous distribution of states available to the conduction electrons, called a band, that extends over the entire solid. Each orbital can be occupied by a pair of electrons with opposite spin, and they are filled in order from lowest to highest orbital in energy. The Fermi energy (EF) is the energy of the most weakly bound electrons. The electrons at the Fermi energy are held in the metal by an energy barrier. Classically, these electrons can never leave the metal unless they are given enough energy to go over this potential barrier. Quantum mechanically, however, electrons near the Fermi energy can tunnel through the potential barrier.

Tunneling

The quantum mechanical phenomenon called tunneling is possible when the tip is only within a few angstroms (10-8 cm) of the surface. Tunneling is the term used to describe the movement of an electron through a classical barrier, which is possible only due to its wave nature and hence impossible in classical physics. To understand this better, consider only one atom. The electrons surrounding the atomic nucleus are not confined to a hard shell but are within a varying probability distribution. This causes the edges of the atom to be indistinct. When the quantum mechanical equations describing the probability of the electron locations are solved, it is found that the electron spends most of its time near the nucleus, and the probability distribution falls off exponentially as the distance from the nucleus increases. Because the electron probability distribution falls off so rapidly with distance from the nucleus, this tunneling current provides a very sensitive probe of interatomic separation. If two atoms are within angstroms of each other, an electron from one atom can move through the region of overlapping electron density to become part of the other atom's electron.

CHALLENGES FOR STM

Theoretically, STM can be used to image individual atoms on the surface; in practice, however, three challenges arise. The first challenge, vibrations, are important because the separation between the sample and probe is so small. Since the tip is only a few angstroms from the surface, it is easy to crash it into the sample unless the substrate is smooth on the atomic scale. For such a small separation, any minor perturbation such as vibrations set up by a sneeze or motion in the room can jam the probe into the sample and ruin the experiment. As a result, careful engineering is necessary to make the instrument rigid and to isolate it from external disturbances.

Another problem, probe sharpness, determines how small a structure can be imaged on the surface. Electrochemical etching can be used to sharpen the end of a metal wire to a radius of about 1000 nm. A probe with such a large surface area would allow tunneling to occur over a large region of the sample surface. In order to detect individual atoms, the probe tip must be comparable in size to an atom. Thus, the probe tip must ideally consist of a single atom. The final problem is that of position control. In order to move the probe with controllable displacements of 0.1 nm (1 angstrom) or less, a special type of piezoelectric ceramic material is used. This material expands and contracts on a scale of angstroms when appropriate external voltages are applied to pairs of electrodes on its opposite faces.

The STM Tip

The tip is prepared so that it terminates in a single atom. The tip is usually composed of tungsten or platinum. If the experiment is performed in a vacuum, tungsten is the preferred material because it is relatively easy to prepare a single-atom-terminated tip.

If the STM experiment is to be performed in a liquid or in air, tungsten reacts too quickly. Therefore, Pt or Pt-Ir alloys are preferred even though it is more difficult to prepare tips with these materials, and they generally are not as atomically sharp.

USES AND CAPABILITIES OF STM

The STM has many uses. It is used in fundamental studies of the physics of atoms at surfaces. STMs can be constructed to be compatible with high-vacuum conditions, which are used to study the properties of atomically “clean” surfaces or surfaces that have been modified in some controlled way. The STM can also be used to study electrode surfaces immersed in liquid electrolytes.

In addition to these scientific applications, the STM has a wide range of potentially practical applications. The STM can image structures ranging from DNA in a biological environment to the surface of an operating battery electrode. The application of the STM to biological molecules has been proposed as a method of gene sequencing. Research is currently being done to demonstrate the ability to write with atomic resolution.

Features a few nanometers wide have been written by using the probe to scratch or dent the surface directly or by using the tunneling current to locally heat the surface of a substance. The probe has even been used to move individual atoms so as to form a word. Scanning tunneling microscopy is a practical demonstration of quantum mechanics. Scanning probe microscopy techniques may be used to create atomic-scale devices and new structures.

For example the STM has been used to prepare a "nanobattery," which consists of two copper pillars and two silver pillars that are placed sequentially on a graphite surface by electrochemical reduction of solutions of copper sulfate and silver fluoride.

SINGLE-CRYSTAL X-RAY DIFFRACTION

The oldest and most precise method of X-ray crystallography is single-crystal X-ray diffraction, in which a beam of X-rays strikes a single crystal, producing scattered beams. When they land on a piece of film or other detector, these beams make a diffraction pattern of spots; the strengths and angles of these beams are recorded as the crystal is gradually rotated. Each spot is called a reflection, since it corresponds to the reflection of the X-rays from one set of evenly spaced planes within the crystal.

For single crystals of sufficient purity and regularity, X-ray diffraction data can determine the mean chemical bond lengths and angles to within a few thousandths of an Ångstrφm and to within a few tenths of a degree, respectively. The atoms in a crystal are also not static, but oscillate about their mean positions, usually by less than a few tenths of an Ångstrφm. X-ray crystallography allows the size of these oscillations to be measured quantitatively.

Procedure

The technique of single-crystal X-ray crystallography has three basic steps. The first — and often most difficult — step is to obtain an adequate crystal of the material under study. The crystal should be sufficiently large (typically larger than 100 micrometres in all dimensions), pure in composition and regular in structure, with no significant internal imperfections such as cracks or twinning. A small or irregular crystal will give fewer and less reliable data, from which it may be impossible to determine the atomic arrangement.

In the second step, the crystal is placed in an intense beam of X-rays, usually of a single wavelength (monochromatic X-rays), producing the regular pattern of reflections. As the crystal is gradually rotated, previous reflections disappear and new ones appear; the intensity of every spot is recorded at every orientation of the crystal. Multiple data sets may have to be collected, with each set covering slightly more than half a full rotation of the crystal and typically containing tens of thousands of reflection intensities.

In the third step, these data are combined computationally with complementary chemical information to produce and refine a model of the arrangement of atoms within the crystal. The final, refined model of the atomic arrangement — now called a crystal structure — is usually stored in a public database.

Limitations

As the crystal's repeating unit, its unit cell, becomes larger and more complex, the atomic-level picture provided by X-ray crystallography becomes less well-resolved (more "fuzzy") for a given number of observed reflections. Two limiting cases of X-ray crystallography are often discerned, "small-molecule" and "macromolecular" crystallography. Small-molecule crystallography typically involves crystals with fewer than 100 atoms in their asymmetric unit; such crystal structures are usually so well resolved that its atoms can be discerned as isolated "blobs" of electron density. By contrast, macromolecular crystallography often involves tens of thousands of atoms in the unit cell. Such crystal structures are generally less well-resolved (more "smeared out"); the atoms and chemical bonds appear as tubes of electron density, rather than as isolated atoms. In general, small molecules are also easier to crystallize than macromolecules; however, X-ray crystallography has proven possible even for viruses with hundreds of thousands of atoms.

CRYSTALLIZATION

Although crystallography can be used to characterize the disorder in an impure or irregular crystal, crystallography generally requires a pure crystal of high regularity to solve for the structure of a complicated arrangement of atoms. Pure, regular crystals can sometimes be obtained from Nature or man-made materials, such as samples of metals, minerals or other macroscopic materials. The regularity of such crystals can sometimes be improved with annealing and other methods. However, in many cases, obtaining a diffraction-quality crystal is the chief barrier to solving its atomic-resolution structure.

Small-molecule and macromolecular crystallography differ in the range of possible techniques used to produce diffraction-quality crystals. Small molecules generally have few degrees of conformational freedom, and may be crystallized by a wide range of methods, such as chemical vapour deposition and recrystallisation. By contrast, macromolecules generally have many degrees of freedom and their crystallization must be carried out to maintain a stable structure. For example, proteins and larger RNA molecules cannot be crystallized if their tertiary structure has been unfolded; therefore, the range of crystallization conditions is restricted to solution conditions in which such molecules remain folded.

Protein crystals are almost always grown in solution. The most common approach is to lower the solubility of its component molecules very gradually; however, if this is done too quickly, the molecules will precipitate from solution, forming a useless dust or amorphous gel on the bottom of the container. Crystal growth in solution is characterized by two steps: nucleation of a microscopic crystallite (possibly having only 100 molecules), followed by growth of that crystallite, ideally to a diffraction-quality crystal. The solution conditions that favour the first step (nucleation) are not always the same conditions that favour the second step. The crystallographer's goal is to identify solution conditions that favour the development of a single, large crystal, since larger crystals offer improved resolution of the molecule. Consequently, the solution conditions should disfavor the first step (nucleation) but favour the second (growth), so that only one large crystal forms per droplet. If nucleation is favoured too much, a shower of small crystallites will form in the droplet, rather than one large crystal; if favoured too little, no crystal will form whatsoever.

It is extremely difficult to predict good conditions for nucleation or growth of well-ordered crystals. In practice, favourable conditions are identified by screening; a very large batch of the molecules is prepared, and a wide variety of crystallization solutions are tested. Hundreds, even thousands, of solution conditions are generally tried before finding one that succeeds in crystallizing the molecules. The various conditions can use one or more physical mechanisms to lower the solubility of the molecule; for example, some may change the pH, some contain salts of the Hofmeister series or chemicals that lower the dielectric constant of the solution, and still others contain large polymers such as polyethylene glycol that drive the molecule out of solution by entropic effects. It is also common to try several temperatures for encouraging crystallization, or to gradually lower the temperature so that the solution becomes supersaturated.

These methods require large amounts of the target molecule, as they use high concentration of the molecule(s) to be crystallized. Due to the difficulty in obtaining such large quantities (milligrams) of crystallisation grade protein, dispensing robots have been developed that are capable of accurately dispensing crystallisation trial drops that are of the order on 100 nanoliters in volume. This means that roughly 10-fold less protein is used per-experiment when compared to crystallisation trials setup by hand (on the order on 1 microliters), Several factors are known to inhibit or mar crystallization.

The growing crystals are generally held at a constant temperature and protected from shocks or vibrations that might disturb their crystallization. Impurities in the molecules or in the crystallization solutions are often inimical to crystallization. Conformational flexibility in the molecule also tends to make crystallization less likely, due to entropy. Ironically, molecules that tend to self-assemble into regular helices are often unwilling to assemble into crystals. Crystals can be marred by twinning, which can occur when a unit cell can pack equally favourably in multiple orientations; although recent advances in computational methods have begun to allow the structures of twinned crystals to be solved, it is still very difficult. Having failed to crystallize a target molecule, a crystallographer may try again with a slightly modified version of the molecule; even small changes in molecular properties can lead to large differences in crystallization behaviour.

Mounting the Crystal

Animation showing the five motions possible with a four-circle kappa goniometer. The rotations about each of the four angles φ, κ, ω and 2θ are shown first. These rotations leave translucent crystal within the X-ray beam, but change the crystal orientation, allowing more of reciprocal space to be observed. Finally, the detector can be slid closer or further away from the crystal, allowing higher resolution data to be taken (if closer) or better discernment of the Bragg peaks.

Once they are full-grown, the crystals are mounted so that they may be held in the X-ray beam and rotated. There are several methods of mounting. Although crystals were once loaded into glass capillaries with the crystallization solution (the mother liquor), a more modern approach is to scoop the crystal up in a tiny loop, made of nylon or plastic and attached to a solid rod, that is then flash-frozen with liquid nitrogen. This freezing reduces the radiation damage of the X-rays, as well as the noise in the Bragg peaks due to thermal motion (the Debye-Waller effect). However, untreated crystals often crack if flash-frozen; therefore, they are generally pre-soaked in a cryoprotectant solution before freezing. Unfortunately, this pre-soak may itself cause the crystal to crack, ruining it for crystallography. Generally, successful cryo-conditions are identified by trial and error.

The capillary or loop is mounted on a goniometer, which allows it to be positioned accurately within the X-ray beam and rotated. Since both the crystal and the beam are often very small, the crystal must be centered within the beam to within roughly 25 micrometres accuracy, which is aided by a camera focused on the crystal. The most common type of goniometer is the "kappa goniometer", which offers three angles of rotation: the ω angle, which rotates about an axis roughly perpendicular to the beam; the κ angle, about an axis at roughly 50° to the ω axis; and, finally, the φ angle about the loop/capillary axis. When the κ angle is zero, the ω and φ axes are aligned. The κ rotation allows for convenient mounting of the crystal, since the arm in which the crystal is mounted may be swung out towards the crystallographer. The oscillations carried out during data collection involve the ω axis only. An older type of goniometer is the four-circle goniometer, and its relatives such as the six-circle goniometer.

X-ray Sources

The mounted crystal is then irradiated with a beam of monochromatic X-rays. The brightest and most useful X-ray sources are synchrotrons; their much higher luminosity allows for better resolution. They also make it convenient to tune the wavelength of the radiation, which is useful for multi-wavelength anomalous dispersion (MAD) phasing, described below. Synchrotrons are generally national facilities, each with several dedicated beamlines where data is collected around the clock, seven days a week.

Smaller, weaker X-ray sources are often used in laboratories to check the quality of crystals before bringing them to a synchrotron and sometimes to solve a crystal structure. In such systems, electrons are boiled off of a cathode and accelerated through a strong electric potential of roughly 50 kV; having reached a high speed, the electrons collide with a metal plate, emitting bremsstrahlung and some strong spectral lines corresponding to the excitation of inner-shell electrons of the metal. The most common metal used is copper, which can be kept cool easily, due to its high thermal conductivity, and which produces strong Kα and Kβ lines. The Kβ line is sometimes suppressed with a thin layer

(0.0005 in. thick) of nickel foil. The simplest and cheapest variety of sealed X-ray tube has a stationary anode (the Crookes tube) and produces circa 2 kW of X-ray radiation. The more expensive variety has a rotating-anode type source that produces circa 14 kW of X-ray radiation.

X-rays are generally filtered to a single wavelength (made monochromatic) and collimated to a single direction before they are allowed to strike the crystal. The filtering not only simplifies the data analysis, but also removes radiation that degrades the crystal without contributing useful information. Collimation is done either with a collimator (basically, a long tube) or with a clever arrangement of gently curved mirrors. Mirror systems are preferred for small crystals (under 0.3 mm) or with large unit cells (over 150 Å)

RECORDING THE REFLECTIONS

When a crystal is mounted and exposed to an intense beam of X-rays, it scatters the X-rays into a pattern of spots or reflections that can be observed on a screen behind the crystal. A similar pattern may be seen by shining a laser pointer at a compact disc. The relative intensities of these spots provide the information to determine the arrangement of molecules within the crystal in atomic detail. The intensities of these reflections may be recorded with photographic film, an area detector or with a charge-coupled device (CCD) image sensor. The peaks at small angles correspond to low-resolution data, whereas those at high angles represent high-resolution data; thus, an upper limit on the eventual resolution of the structure can be determined from the first few images. Some measures of diffraction quality can be determined at this point, such as the mosaicity of the crystal and its overall disorder, as observed in the peak widths. Some pathologies of the crystal that would render it unfit for solving the structure can also be diagnosed quickly at this point.

One image of spots is insufficient to reconstruct the whole crystal; it represents only a small slice of the full Fourier transform. To collect all the necessary information, the crystal must be rotated step-by-step through 180°, with an image recorded at every step; actually, slightly more than 180° is required to cover reciprocal space, due to the curvature of the Ewald sphere. However, if the crystal has a higher symmetry, a smaller angle such as 90° or 45° may be recorded. The axis of the rotation should generally be changed at least once, to avoid developing a “blind spot” in reciprocal space close to the rotation axis. It is customary to rock the crystal slightly (by 0.5-2°) to catch a broader region of reciprocal space.

Multiple data sets may be necessary for certain phasing methods. For example, MAD phasing requires that the scattering be recorded at at least three (and usually four, for redundancy) wavelengths of the incoming X-ray radiation. A single crystal may degrade too much during the collection of one data set, owing to radiation damage; in such cases, data sets on multiple crystals must be taken.

X-RAY POWDER DIFFRACTION

X-RAY ANALYTICAL METHODS

X-rays were discovered by W.C. Rφentgen in 1895, and led to three major uses:

- X-ray radiography is used for creating images of light-opaque materials. It relies on the relationship between density of materials and absorption of x-rays. Applications include a variety of medical and industrial applications.
- X-ray crystallography relies on the dual wave/particle nature of x-rays to discover information about the structure of crystalline materials.
- X-ray fluorescence spectrometry relies on characteristic secondary radiation emitted by materials when excited by a high-energy x-ray source and is used primarily to determine amounts of particular elements in materials.

This course is primarily concerned with the x-ray crystallography of powders. In course materials you will commonly find X-ray Diffraction, X-ray powder diffraction, and the abbreviation XRD used interchangeably. Though intellectually somewhat sloppy, it is also common practice.

Uses of X-Ray Powder Diffraction

The most widespread use of x-ray powder diffraction, and the one we focus on here, is for the identification of crystalline compounds by their diffraction pattern.

Listed below are some specific uses that we will cover in this course:

- Identification of single-phase materials – minerals, chemical compounds, ceramics or other engineered materials.
- Identification of multiple phases in microcrystalline mixtures (*i.e.*, rocks)
- Determination of the crystal structure of identified materials
- Identification and structural analysis of clay minerals
- Recognition of amorphous materials in partially crystalline mixtures

Below are some more advanced techniques. Some of these will be addressed in an introductory fashion in this course.

Many are left for more advanced individual study:

- Crystallographic structural analysis and unit-cell calculations for crystalline materials.
- Quantitative determination of amounts of different phases in multi-phase mixtures by peak-ratio calculations.
- Quantitative determination of phases by whole-pattern refinement.
- Determination of crystallite size from analysis of peak broadening.
- Determine of crystallite shape from study of peak symmetry.

- Study of thermal expansion in crystal structures using in-situ heating stage equipment.

XRD FOR DUMMIES

The physics and mathematics describing the generation of monochromatic X-rays, and the diffraction of those X-rays by crystalline powders are very complex (and way beyond my limited abilities to expound upon them). Fortunately a complete understanding of the mathematics involved is not required to obtain, interpret and use XRD data. What is required is a basic understanding of how the X-rays interact with your specimen, the sources and characteristics of possible errors, and what the data tell you about your sample1. What follows is a generalized explanation of the process of going from X-rays to diffraction data for math-challenged geologists like me. Some of these processes will be treated a bit more rigorously later in the course. For those who want to delve into the physics of X-ray diffraction.

The intent here is to provide a conceptual framework for what is happening:

- The X-ray tube
- The flat specimen (labeled sample in the diagram)
- The goniometer circle (labeled measuring circle in the diagram) which remains constant through the analysis and is defined by the position of the target (Cu in our system) in the X-ray tube, the center of the sample,

and the position of the receiving slit (labeled detector diaphragm) on the detector side.

- The X-ray tube, specimen and receiving slit also lie on the arc of the focusing circle. Unlike the goniometer circle which remains fixed, the radius of the focusing circle is a function of θ-2θ, with the radius decreasing as θ increases.
- The incident angle θ defined as the angle between the incident beam and the sample, and 2θ defined as the angle between the incident and diffracted beams. The detector is moved (rotated) at twice the angular rate of the sample to maintain the θ-2θ geometry.
- A filter (on the diffracted beam side) is used (in this example) to remove all but the desired Kα radiation from the diffracted beam before it enters the detector.
- A slit (labeled aperture diaphragm) on the incident beam side is used to narrow the beam so that it is confined within the area of the specimen.
- The path AB=BC is the radius of the diffractometer circle.
- The tube position is fixed and the θ-2θ geometry is maintained by rotating the sample holder at ½ the angular rate of the detector.
- There are Soller slits on both the tube and detector side, and two collimating and receiving slits.

- Note the easy-to-read angular indicators and micrometer dials for visually reading θ and 2θ.
- The detector on this system also includes a graphite monochromator adjacent to the scintillation detector (off the photo, top right) eliminating the need for any filters in the system.

Sample Preparation

The Ideal Specimen is a statistically infinite amount of randomly oriented powder with crystallite size less than 10 µm, mounted in a manner in which there is no preferred crystallite orientation. In this day of automated data collection and analysis, the preparation of your specimen is usually the most critical factor influencing the quality of your analytical data. Sample preparation is a significant topic in this course.

GENERATE ANALYTICAL X-RAYS

A coherent beam of monochromatic X-rays of known wavelength is required for XRD analysis Striking a pure anode of a particular metal with high-energy electrons in a sealed vacuum tube generates X-rays that may be used for X-ray diffraction. By the right choice of metal anode and energy of accelerated electrons, a known wavelength (*i.e.*, energy) or group of wavelengths will dominate the X-rays generated. Copper (Cu) X-ray tubes are most commonly used for X-ray diffraction of inorganic materials. The wavelength of the strongest Cu radiation (Kα) is approximately 1.54 angstroms (Å). Other anodes commonly used in X-ray generating tubes include Cr (Kα 2.29 Å), Fe (Kα 1.94 Å), Co (Kα 1.79 Å), and Mo (Kα 0.71 Å).

The full spectrum of radiation produced, and how it is "processed" to get to a (more or less) monochromatic character will be discussed in more detail later. For most X-ray diffraction applications, the closer we can get to monochromatic radiation in our X-ray beam, the better our experimental results will be. The radiation produced in the tube includes Kα1, Kα2, and Kβ as the highest energy X-rays and a whole host of lower energy radiation. We generally use the Kα for our analytical work. The Kβ radiation is usually removed by use of a filter, a monochromator or an energy-selective detector. The Kα2 radiation is removed from the X-ray data electronically during data processing.

DIRECT THE X-RAYS AT A POWDERED SPECIMEN

An approximately parallel beam of X-rays is directed at the powdered specimen. In most powder diffractometers systems a series of parallel plates (soller slits) arranged parallel to the plane of the diffractometer circle and several scatter and receiving slits (arranged perpendicular to the diffractometer circle) are used to create an incident beam of X-rays that are (approximately) parallel. Soller slits are commonly used on both the incident and diffracted beam, but this will vary depending on the particular system.

The scatter slits (on the incident beam side) may be varied to control the width of the incident beam that impinges upon the specimen and the receiving slits may be varied to control the width of the beam entering the detector. Filters for removing Kβ may be located in the beam path on the generator or detector side of the path; a monochromator, if present, is usually located on the detector side between the receiving slit and the detector. The newest diffractometers may be purchased with sophisticated (usually of a very proprietary nature) optical systems that can create a tightly controlled and focused incident beam of X-rays.

MEASURE X-RAYS "DIFFRACTED" BY THE SPECIMEN AND OBTAIN A DIFFRACTION PATTERN

Interaction of X-rays with sample creates secondary "diffracted" beams (actually generated in the form of cones) of X-rays related to interplanar spacings in the crystalline powder according to a mathematical relation called "Bragg's Law":

$$n\lambda = 2d \sin\theta$$

Where:

- n is an integer
- λ is the wavelength of the X-rays
- d is the interplanar spacing generating the diffraction and
- θ is the diffraction angle

- λ and d are measured in the same units, usually angstroms.

We will derive the Bragg law a bit more rigorously later but for a powder specimen in a diffractometer having a statistically infinite amount of randomly oriented crystallites, diffraction maxima (or peaks) are measured along the 2θ diffractometer circle.

Powder diffractometers come in two basic varieties: θ-θ in which the X-ray tube and detector move simultaneously or a θ-2θ in which the X-ray tube is fixed, and the specimen moves at ½ the rate of the detector to maintain the θ-2θ geometry. Our Scintag PAD V system is a θ-2θ system; the Siemens D5000 systems located in the Chemistry Department are θ-θ systems. In both systems the geometry shown in the previous diagrams is maintained during data collection.

The "angle" of the diffraction (recorded as 2θ by convention) is related to the interplanar spacing, d, by the Bragg law, and the intensity of the diffraction maximum is related to the strength of those diffractions in the specimen. The angles and intensities of diffractions are recorded electronically using a detector, electronics and specialized software resulting in a plot of 2θ (horizontal axis) vs. intensity (vertical axis) for the specimen.

Detectors

There are a variety of detectors used in XRD systems. The Scintag system in our laboratory uses a scintillation counter.

In the Chemistry XRD lab, the Siemens systems have either scintillation counters or a large-window position sensitive detector or PSD (covering 8° 2θ simultaneously). Scintillation counters are some of the oldest technology available, but are still widely used because of their relatively low cost, ease of use and durability.

Newer detector technologies can deliver improved quality data, a higher degree of energy selectivity or deliver it faster. All detector technologies also involve tradeoffs in cost and/or maintenance. We will briefly discuss detector technologies later in the course.

"Legacy" Methods

Before the advent of computerized data collection, X-ray diffraction data were derived by film methods or by diffractometers using paper strip-chart recorders. In both cases, the resultant data were derived by physically measuring peak positions and intensities, and the diffraction data recorded as a list of peaks (in degrees 2θ) and relative intensities (scaled from 0 to 100). Modern automated diffractometers and the associated automation software collect data electronically, process and calculate it digitally removing much of the tedium from the acquisition of powder XRD data.

Some of the "legacy" methods are useful for understanding the process of diffraction, and we will address some of these in this course.

DETERMINE THE CRYSTALLINE PHASES PRESENT IN THE SPECIMEN

For most samples, the aim of the analysis is to identify the crystalline phases present. Even for work where other information is sought (*i.e.*, unit cell calculations, quantitative determinations, etc.), identification of the phase(s) present is usually the first step. Phase identification is accomplished by comparing the data (peaks and relative intensities) from your specimen with peaks and relative intensities from a very large set of "standard" data provided by the International Center for Diffraction Data (ICDD). The current PDF4 release contains 254,873 Digital XRD patterns, both experimental and calculated, from almost every known inorganic and many organic crystalline substances.

In our lab we use Jade to facilitate the access to this massive (and continually growing) database. Jade includes an automated search-match function that compares the sample pattern with the ICDD database. With good data from a single-phase sample, Jade's automated search-match programme will usually identify the phase successfully with little or no effort on your part. For most two-phase samples identification of the dominant phase will usually be successful, but the second may require more hunting. With three or more phases (and virtually all bulk rocks), some knowledge of the likely constituents will be required to successfully "sleuth" the constituents. Fortunately the ability to visually compare your sample pattern to a large number of possible phases is a manageable task. We will spend considerable laboratory time learning to use this powerful software. Prior to the advent of automated XRD software like Jade, manual methods required the listing of all the 2θ-intensity values for your sample and the use of paper indexes to identify phases.

2

Solid State Chemistry

CHEMICAL BONDS

Before Dalton's atomic theory there wasn't much reason to consider how atoms stick together, although it was clear that some force is necessary to bind compounds of elements together.

The term "chemical affinity" referred more to the ability to react (undergo a chemical change) than to form a stable compound. When it was realised that chemical compounds were formed of discrete molecules containing fixed numbers of atoms, the need to explain molecular stability developed, leading to the notion of the interatomic chemical bond (Latin inter for among plus band for a fastening) holding atoms together.

Early Nineteenth Century speculations about the origin of interatomic bonds were affected by contemporary discoveries in electricity, indicating that "opposites" attract. Positive and negative charges are electrical opposites, and north and south poles are magnetic opposites. Precisely just what constituted chemical opposites wasn't clear, however. Chemists had classified substances into metals and non-metals, and into acids and bases, both of which seemed opposite in the sense that they had "affinity" for each other and readily reacted together to form new compounds.

Yet there was little evidence to support the hypothesis of Avogadro that non-metal gases were composed of two atoms of the same element, nor were there any explanations for the solid state of metallic elements, or the extreme hardness of non-metallic elements such as diamond. The number of bonds an element could make, called the valence (Latin valere for strength) of the element, is suggested by the atom ratios of chemical formulas, and ordinarily limited to a small number. For example, hydrogen atoms never forms bonds to more than one another atom, so are assigned a valency of one.

Oxygen has a valency of two (is divalent) as each oxygen atom combines with two hydrogen atoms in forming water (H2O, more descriptively written showing atom connections as H-O-H). Carbon has a valency of four (is tetravalent) because it combines with a maximum of four hydrogen atoms (in methane, CH4 more descriptively shown with C surrounded by 4 H), or, equivalently, a maximum of two oxygen atoms, each with a valency of two (in carbon dioxide, CO2, more descriptively written O-C-O).

The electrons of atoms are electromagnetically attracted by the nuclei of atoms, due to the opposite electric charge of electrons and nuclei. Chemical bonds are characterised by physical states in which a few electrons move partly from one atom to one or more other atoms, driven by the achievement of a lower state of energy from this motion.

This lowering of energy is caused by a rearrangement of charges, usually resulting in net decrease in the average distance between the electrons of all the bonded atoms, and their nuclei. The transfer of charge caused by the movement of the electron from one atom to another, also causes the participating atoms (which may number from two to many) to be attracted to one another electromagnetically. The attractive force between atoms is the bond. Chemical bonds, for the sake of simplicity, are classically assigned characteristics of two major types: covalent and ionic.

In a simplified view of a pure covalent type bond, the bond forms as a few electrons farthest from their atomic nuclei become more attracted to the region of space between two nuclei. In this region, negatively-charged electrons experience attraction from the positively-charged protons from more than one nucleus. This causes some electrons to spend a high probability of their time in the interatomic space. In turn, the nuclei are stabilized in position by the pull from these shared electrons during the fraction of time that the bonding electrons reside between the atoms. Although such bonding electrons do not spend all of their time between atoms, when they spend more time between a given pair of atoms than otherwise, they constitute chemical bonds. Nuclei fixed by such bonds may vibrate, but they are pulled towards each other by the mutual forces of the bonding electrons pulling them together, yet prevented from approaching too closely by their own charge, or else by the mutual repulsion of other inner electrons, which are held so closely and tightly to individual nuclei that they cannot be shared to any important degree.

In a simplified view of a pure ionic type bond, one or more outer electrons are not shared between atoms, but donated from one atom to another. In such a bond, the structure of the electron cloud of one of the nuclei contains an available space for another electron, which allows an additional electron to experience a greater net attraction from the nucleus than is experienced by outer electrons in a neighboring atom towards their own nucleus.

This difference in available states causes effective transfer of one or more electrons from one atom to another atom, where they can be more tightly bound. This transfer causes the donating atom to assume a net positive charge, and the other to assume a net negative charge; the atoms thus become positive or negatively charged ions. The bond then results from electrostatic attraction between these ionized atoms.

Most bonds have a mixture of covalent and ionic character, as bonding electrons are shared between atoms, but shared somewhat unevenly. All bonds can be explained by quantum theory, but in practice, simplification rules allow chemists to predict the strength, directionality, and polarity of bonds. The octet rule and VSEPR theory are two examples. More sophisticated theories are valence bond theory which includes orbital hybridization and resonance, and the linear combination of atomic orbitals molecular orbital method which includes ligand field theory. Electrostatics are used to describe bond polarities and the effects they have on chemical substances.

IONIC AND COVALENT CHEMICAL BONDS

Chemical salts are found to conduct electricity when melted or dissolved in water, suggesting the presence of charge carriers, called ions (from the Greek for traveller). Since salts are neutral compounds, the charge carriers must be divided into two groups, one positively charged and the other negatively charged. The oppositely charged ions would be bound through electrostatic attractions, or ionic bonds. Because chemical salts are known to be composed of metallic elements bound to non-metallic elements, the most reactive of which are found at opposite ends of the periodic table, ionic attraction can be explained in terms of the attraction of opposites.

When metals or nonmetals bond to elements of their own kind, the reason for the bonding is not so obvious. Compounds containing different elements might have some attraction due to the differences between the elements, but homonuclear (one-element) polyatomic (more than one atom) elements such as H2 or sodium metal are bound by some common feature rather than by some difference between the atoms. Such bonds, called covalent bonds (Latin co + valere for joint strength), are not limited to homonuclear molecules but also occur between atoms of different elements that are close in behaviour. The periodic table summarizes the properties of the elements, including bonding trends as well, and can be used to decide the basic type of bonding between atoms in molecules in a binary.

Ionic Bonds

Ionic bonds are simply the attractive forces between oppositely-charged ions. Ionic compounds contain cations (which can be either monatomic or polyatomic) and anions (which can be either monatomic or polyatomic.) Remember that ions are formed by the loss or gain of electrons. For monatomic cations, the electrons which are lost first in the formation of the ion are always the outermost (valence) electrons. For example, you already know that the 4s subshell is at lower energy than the 3d subshell in a neutral atom.

This is why the 4s subshell fills before the 3d. For ions, however, the order of orbital energies approaches that for a hydrogen ion, where all subshells in a given main shell have the same energy. For this reason, the 4s electrons are lost before the 3d electrons when a cation is formed from a transition metal. For example, the configuration of a neutral cobalt atom is [Ar]4s23d7, but the configuration of a cobalt(III) ion is [Ar]3d6.

A simple view of the formation of an ionic compound is that the electrons lost by the cation are gained by the anion; in other words, a formal transfer of electrons can be envisioned. This is why the total positive charge from the cations must be balanced by the total negative charge from the anions - no free electrons are floating around. This gives rise to the formula Al2O3 for aluminum oxide rather than AlO3, AlO, Al3O2, or other incorrect formulas.

ELECTRONEGATIVITY

Electronegativity is a measure of the tendency of an atom to attract the bonding electrons in a chemical bond towards itself. It is not a precisely-defined quantity like ionization potential or electron affinity, which can be measured accurately. In fact, there are more than a dozen scales of electronegativity. Luckily, for introductory courses only one scale is really needed to put the concept to use: this is the Pauling scale, named after the two-time Nobel prize winning chemist Linus Pauling.

According to this scale, fluorine is the most electronegative element, with a Pauling electronegativity of 4.0. The least electronegative element is cesium, with a Pauling electronegativity of 0.7. Thus, there is a range of about 3.3 Pauling units between the electronegativities of the most and least electronegative elements. Be sure you understand the two periodic trends in electronegativity and the rule for getting the electronegativity of any second-period element just by memorizing the value of 4.0 for fluorine:

- Electronegativity increases from left to right in a given period.
- Electronegativity decreases from top to bottom in a given group.

To get the electronegativity of a second-period element, start at fluorine (4.0) and subtract 0.5 Pauling unit for each step to the left in the second period. Thus, oxygen has an electronegativity of 3.5, nitrogen has an electronegativity of 3.0, etc. Sometimes a table of electronegativities is used to classify the possible bonds between each pair of atoms in a molecule into two categories, ionic or covalent. Bonds between atoms which differ in electronegativity on a scale of 0 to 4 by more than 2 units may be assumed to be ionic. However, since electronegativities of metals vary between 1 and 2 and non-metals between 2 and 4, metal to non-metal bonds are the only ionic bonds. Electronegativities are useful for more refined classifications and trends in terms of the per cent ionic or covalent character of a bond.

In these terms, ionic bonds are those with more than 50% ionic character.2 Because electronegativity is only a semiquantitative concept, there is no simple equation relating electronegativity to per cent ionic or covalent character, and there is no standard table of electronegativities. This is due to the fact that atoms in molecules are only approximately localized and independent of the environment of the entire molecule. This prevents assigning unique electronegativities to atoms which experience a variety of bonding environments. A parameter used to indicate the charge an atom has or would have if it were ionized in compounds is the oxidation number. Three rules help define the assignment of oxidation numbers to atoms in compounds.

Covalent Bonds

Covalent bonds are bonds formed by the sharing of electrons, in contrast to the transfer which can be envisioned for an ionic bond. Covalent bonds are formed when the electronegativity difference between the two elements involved in the bond is small, indicating that the two atoms have similar attractions for the electrons. On the other hand, large differences in electronegativities give rise to ionic bonds. Half of the range (3.3) of Pauling electronegativity values is about 1.7. This value can be used as a ballpark dividing line between ionic and covalent bonds: if the difference in electronegativities between the two atoms is greater than 1.7, then the bond is predominately ionic; if the difference is less than 1.7, then it is predominately covalent; if it is 1.7, then the bond has approximately 50% ionic and 50% covalent character. It is unusual, however, that you'll need to make such quantitative determinations, especially since they are only approximate. For example, the electronegativity difference between Li and I is 2.5-1.0, or 1.5.

This would imply more covalent than ionic character, but most chemists would classify lithium iodide as an ionic compound because it is composed of a metal and a nonmetal. Ionic compounds are formed between metals and nonmetals, whereas covalent compounds are formed between nonmetals. The simple reason is that metals are on the left side of the periodic table and nonmetals are on the right side, giving a fairly large difference in electronegativities. Nonmetals, on the other hand, are in the same general region of the periodic table and thus there are small electronegativity differences between two nonmetals.

The only purely covalent compounds are those where the electronegativity difference is zero - and this occurs for homonuclear diatomic molecules like N2, O2, H2, etc. One final clarification is necessary: the bonding within a polyatomic ion is covalent, since the atoms in the ion are nonmetals (NH4+, SO42-, etc.). But compounds of these ions are ionic, since by definition an ionic bond is the electrostatic attraction between oppositely-charged ions in the crystal. Thus, sodium nitrate, NaNO3, is an ionic compound, but the bonding within the nitrate ion is covalent.

POLAR MOLECULES

You already know that covalent bonds represent shared electrons. This does not necessarily mean, however, that the electrons are shared equally. An unequal sharing of electrons results in a polar covalent bond (sometimes simply called a polar bond.) Such a bond results in a partial negative charge at one end of the bond and a partial positive charge at the other end. If a molecule consists of only one bond and the bond is polar, then the molecule must be polar. Examples of this situation are HF, HCl, ClF, etc. The partial negative charge resides on the end of the bond with the more electronegative atom, while the partial positive charge resides on the end with the less electronegative atom. The partial negative charge in the three molecules above is at the end with F, Cl, and F, respectively.

If a molecule has more than one bond, then the molecule as a whole is nonpolar only if the individual polarities of the bonds cancel each other. To decide if this happens, the geometry of the molecule must be known. For example, the carbon dioxide molecule is linear, with each C-O bond along the same line: O=C=O. Although each carbon-oxygen bond is polar, the molecule as a whole is nonpolar because the two equal polarities are in exactly opposite directions. Water, on the other hand, is a bent molecule. The two H-O polar bonds do not cancel each other, and as a result the molecule is polar. Three molecules which have polar bonds but which have no molecular dipole moment because the individual bond polarities cancel one another. The topic of molecular geometry is discussed in section 8.13 (and at the end of this document), which describes the VSEPR model.

COVALENT BOND ENERGIES

Bonds are stable because the ions in an ionic bond are at lower energy when they are close to one another in the crystal, and because the shared electrons in a covalent bond are attracted by the two nuclei of the bonded atoms. Thus, it takes energy to break ionic and covalent bonds. Covalent bond energies are average energies, each of which depends on the chemical environment of the bonded atom. For example, the successive bond dissociation energies for methane are shown on page 366 of the text. Although the four values (one for each C-H bond) are slightly different, their average value of 413 kJ/mol can be assumed to represent the energy of a covalent carbon-hydrogen bond. A number of bond energies are shown in Table 8.4. Notice that the table is separated into single bond and multiple bond categories. Table 8.5 lists bond lengths for selected bonds. Notice that for a given pair of atoms, bond length decreases in the order,

single > double > triple.

Since the formation of covalent bonds releases energy and the breaking of bonds requires energy, we can calculate the approximate the enthalpy change for a chemical reaction by using tabulated bond energies. The procedure is simple: first, break apart all the bonds in the reactants and determine how much energy is required (this is endothermic, and thus a positive value.) Then determine how much energy is released when the bonds in the products form (this is exothermic, and thus a negative value.) Add the two quantities to get the enthalpy change for the reaction.

Important note: It is essential that the type of bonds in the reactants and products are known. For example, simply looking at the formula N2 might give one the impression that a single-bond N-N energy of 160 kJ per mole should be used. However, this will result in an incorrect answer, since there is a triple bond in the nitrogen molecule with a covalent bond energy of 941 kJ/mole. The types of bonds in a molecule can be determined by drawing the Lewis electron-dot structure for the molecule.

Resonance

Although Lewis structures are very useful for a large number of molecules, there are some problems with using electron-dot structures to describe bonding:

One of the goals in drawing a Lewis structure is to pair up electrons. This is impossible for a molecule with an odd number of electrons, like NO or ClO2. Which atom "has" the odd electron in these molecules?

Another goal for obtaining a valid Lewis structure is to obtain a duet of electrons around hydrogen or a completed octet around other atoms. The fact, however, is that there are exceptions to the octet rule: Be in BeF2 and B in BF3 have only four and six electrons in the Lewis structure, respectively, instead of eight. Atoms in the third period and below are able to "expand" their octet and can thus have more than eight electrons in the Lewis structure. Some examples are SF4 (10 e- around sulfur) and XeF4 (12 e- around xenon). There are many more examples.

Sometimes a single Lewis structure for a molecule doesn't accurately explain the properties of the molecule. For example, the Lewis structure for sulfur dioxide, SO2, has a single sulfur-oxygen bond, a double sulfur-oxygen bond, and a lone pair of electrons on the central sulfur atom. All electrons are paired, 18 valence electrons are used in the Lewis structure, and each atom has an octet. Thus, the Lewis structure is "correct", at least in a formal sense. The problem is that the electron-dot diagram implies that there should be two bond strengths in sulfur dioxide - an S-O single bond and a stronger S-O double bond. Furthermore, there should also be two different bond lengths - a longer S-O single bond and a shorter S-O double bond. Here's the problem: experimentally, it has been found that both sulfur-oxygen bonds have the same bond length and the same bond strength. The concept of resonance is used to overcome this sort of problem with Lewis structures.

The problem mentioned above is not a problem with the molecule - it is a problem with the limited ability of a simple notation like a Lewis structure to describe a complicated concept like the bonding in a molecule. It is rather like trying to describe a real, three-dimensional object by drawing it on a two-dimensional piece of paper; the problem isn't with the object - it is with our limited resources for making the drawing.

The best way to describe the bonding in molecules like SO2 is to draw two or more Lewis structures and say that the actual molecule is a hybrid, or combination, of the separate structure; this is indicated by drawing double-headed arrows between the structures.

Each of the separate structures is called a resonance structure, and the actual molecule is described as a resonance hybrid of the resonance structures. It is important to remember two rules for drawing resonance structures: The positions of all atoms in all resonance structures of a given molecule must be the same. In other words, atoms are not moved when a different resonance structure is drawn from an existing one; rather, electron pairs are moved. Do not think that the actual structure results from an oscillation among the resonance structures. For example, each of the two resonance structures for sulfur dioxide has a single bond and a double bond: the difference is in the location of each.

Don't think that at a particular instant there is a single bond between the sulfur and one of the oxygens and that in the next instant the bond becomes a double bond, with continual "flipping" back and forth. This is not the correct interpretation of resonance. Both bonds in SO_2 are identical, and the bonds are neither single nor double bonds. Each bond has properties intermediate between a single and double bond. The resonance hybrid can be compared to a mule, which is a hybrid between a horse and a donkey. The mule has its own unique properties, and it exists in its own right — it isn't a horse half the time and a donkey the other half of the time.

Formal Charge

Unlike oxidation number, which can be determined from a formula like Na_2SO_4, the formal charge of an atom in a covalent molecule or polyatomic ion can only be determined from the Lewis structure. Formal charge is calculated by splitting the bonding electrons equally between the bonded atoms, and assigning all nonbonding electrons to the atom which "owns" them, then comparing the resulting number of electrons with the number of valence electrons the atom would have if it were neutral. Formal charges are shown as a positive number or negative number (*e.g.* +2 or –1) inside a circle and placed next to the atomic symbol in the Lewis structure. Recall that oxidation numbers are written without the circle.

For example, the Lewis structure for carbon dioxide shows two carbon-oxygen double bonds and two nonbonding pairs of electrons on each of the oxygen atoms. The carbon atom has four bonding pairs of electrons (two double bonds, or eight electrons) around it. The central carbon atom is assigned four of these eight electrons and each oxygen is assigned two of them. The formal charge of carbon is therefore number of valence electrons minus number of electrons after assignment, or 4 minus 4 = a formal charge of zero. Each oxygen atom "owns" two nonbonding pairs of electrons (four electrons) and was assigned two of the bonding electrons, giving a total of six electrons. The formal charge is therefore 6-6= a formal charge of zero. Now draw one of the resonance structures for sulfur dioxide, with one S-O single bond, one S-O double bond, and a nonbonding pair on the central sulfur atom (remember to complete the octets around the oxygen atoms.) Assigning the electrons as described above leads to a formal charge of +1 for the sulfur, -1 for the singly-bonded oxygen and zero for the doubly-bonded oxygen.

Let's look at one more example. Draw the Lewis structure for the sulfate ion, $(SO_4)^{2-}$, which has four single sulfur-oxygen bonds. Verify the formal charges of +2 for the central sulfur atom and -1 for each of the oxygen atoms. Notice that in the CO_2, SO_2, and $(SO_4)^{2-}$ examples above, the algebraic sum of the formal charges is equal to the charge on the molecule or ion. This must always be the case. Remember that formal charges cannot be determined from a simple formula; the Lewis structure is needed.

Formal Charges and Resonance

Formal charges can be used to decide if a particular resonance structure is a "good" one - in other words, if the resonance structure contributes significantly to the actual structure.

Here are the rules:

- "Like" formal charges (plus/plus or minus/minus) should not reside on adjacent atoms.
- "Unlike" formal charges (plus/minus) should not be unnecessarily separated.

Formal charges closer to zero usually represent more important resonance structures than those which have large formal charges. For example, draw one of the Lewis structures for nitrous oxide (laughing gas, N2O - the skeletal structure is N-N-O). You should now be able to "push" electron pairs around to come up with a total of three resonance structures which obey the octet rule. Each of these resonance structures. Make sure you correctly determined these formal charges for all three of the resonance structures (Formal charges are listed in the following order: terminal nitrogen, central nitrogen, oxygen.)

- N-N double bond, N-O double bond: formal charges are –1, +1, 0.
- N-N triple bond, N-O single bond: formal charges are 0, +1, and -1.
- N-N single bond, N-O triple bond: formal charges are –2, +1, and +1.

According to the rules mentioned above, resonance structures 1 and 2 are "good" structures and contribute significantly to the actual structure. Resonance structure 3 results in the placement of two positive formal charges on adjacent atoms, and thus does not contribute significantly to the actual structure.

THE VSEPR MODEL

According to the Valence Shell Electron Pair Repulsion model, the geometry of a molecule or polyatomic ion is determined by repulsions between valence electron pairs in the molecule. The idea is simple: since electrons all have the same charge, electron pairs repel each other, resulting in a geometry in which these mutual repulsions are minimized. The overall geometry is determined by the total number of "groups" around the central atom in the species. A "group" is any of the following: a single bond, double bond, triple bond, or nonbonding pair.

The molecular geometry is obtained by first determining the overall geometry, then ignoring any nonbonding pairs around the central atom and deciding what shape results. A common abbreviation for representing a molecule or ion uses the symbol A for the central atom, X for an atom bonded to the central atom, and E for a nonbonding pair on the central atom. For example, methane (CH4) can be represented by the general abbreviation AX4, while ammonia (NH3) and water can be generalized as AX3E and AX2E2 types, respectively.

The following table lists some examples.

Type	**Overall Geometry**	**Molecular Geometry**	**Examples**
AX2	Linear	Linear	BeF2, CO2
AX3	Trigonal planar	Trigonal planar	BCl3, H2CO
AX2E	Trigonal planar	Bent, angular, or V-shaped	SO2
AX4	Tetrahedral	Tetrahedral	CH4, (SO4)2-
AX3E	Tetrahedral	Trigonal pyramidal	NH3
AX2E2	Tetrahedral	Bent, angular, or V-shaped	H2O
AX5	Trigonal bipyramidal	Trigonal bipyramidal	PCl5
AX4E	Trigonal bipyramidal	Seesaw or distorted Tetrahedral	SF4
AX3E2	Trigonal bipyramidal	T-shaped	ClF3
AX2E3	Trigonal bipyramidal	Linear	XeF2
AX6	Octahedral	Octahedral	SF6
AX5E	Octahedral	Square pyramidal	IF5
AX4E2	Octahedral	Square planar	(BrF4)-, XeF4

Remember the following rules about using VSEPR to describe molecular geometries: Electron pair repulsions decrease in the order (nonbonding-nonbonding) > (nonbonding-bonding) > (bonding-bonding) and triple bond > double bond > single bond

Nonbonding pairs occupy equatorial (radial) positions in a trigonal bipyramid. Two nonbonding pairs in an overall octahedral structure occupy trans positions (across from one another)

Bond angles decrease with increasing electronegativity of the non-central atoms, provided that there is at least one nonbonding pair in the species. For example, the F-N-F bond angle in NF3 is smaller than the H-N-H bond angle in ammonia. A simple way to understand this is to picture the bonding electrons in NF3 as being closer to the more electronegative fluorine than the nitrogen, thereby allowing the nonbonding pair to "squeeze" the bonding pairs closer together, resulting in a smaller bond angle. In ammonia, the bonding electrons are closer to the more electronegative nitrogen than the hydrogen, and are therefore already close to one another. This doesn't allow the nonbonding pair to push the hydrogens as close together as it could for the fluorine atoms in NF3.

VALENCE BOND THEORY

Valence bond theory was formulated which argued essentially that a chemical bond forms when two valence electrons, in their respective atomic orbitals, work or function to hold two nuclei together, by virtue of system energy lowering effects. In 1931, building on this theory, chemist Linus Pauling published what some consider one of the most important papers in the history of chemistry: "On the Nature of the Chemical Bond". In this paper, building on the works of Lewis, and the valence bond theory (VB) of Heitler and London, and his own earlier work, he presented six rules for the shared electron bond, the first three of which were already generally known:

1. The electron-pair bond forms through the interaction of an unpaired electron on each of two atoms.

2. The spins of the electrons have to be opposed.
3. Once paired, the two electrons cannot take part in additional bonds.

His last rules were new:

- The electron-exchange terms for the bond involves only one wave function from each atom.
- The available electrons in the lowest energy level form the strongest bonds.

Of two orbitals in an atom, the one that can overlap the most with an orbital from another atom will form the strongest bond, and this bond will tend to lie in the direction of the concentrated orbital.

Building on this article, Pauling's 1939 textbook: On the Nature of the Chemical Bond would become what some have called the "bible" of modern chemistry. This book helped experimental chemists to understand the impact of quantum theory on chemistry.

However, the later edition in 1959 failed to address adequately the problems that appeared to be better understood by molecular orbital theory. The impact of valence theory declined during the 1960s and 1970's as molecular orbital theory grew in popularity and was implemented in many large computer programmes. Since the 1980s, the more difficult problems of implementing valence bond theory into computer programmes have been largely solved and valence bond theory has seen a resurgence.

MOLECULAR ORBITAL THEORY

Molecular orbital theory (MO) uses a linear combination of atomic orbitals to form molecular orbitals which cover the whole molecule. These are often divided into bonding orbitals, anti-bonding orbitals, and non-bonding orbitals. A molecular orbital is merely a Schrφdinger orbital which includes several, but often only two nuclei. If this orbital is of type in which the electron(s) in the orbital have a higher probability of being between nuclei than elsewhere, the orbital will be a bonding orbital, and will tend to hold the nuclei together.

If the electrons tend to be present in a molecular orbital in which they spend more time elsewhere than between the nuclei, the orbital will function as an anti-bonding orbital and will actually weaken the bond.

Electrons in non-bonding orbitals tend to be in deep orbitals (nearly atomic orbitals) associated almost entirely with one nucleus or the other, and thus they spend equal time between nuclei or not. These electrons neither contribute nor detract from bond strength.

Comparison of Valence Bond and Molecular Orbital Theory

In some respects valence bond theory is superior to molecular orbital theory. When applied to the simplest two-electron molecule, H2, valence bond theory, even at the simplest Heitler-London approach, gives a much closer approximation to the bond energy, and it provides a much more accurate representation of the behaviour of the electrons as chemical bonds are formed and broken. In contrast simple molecular orbital theory predicts that the hydrogen molecule dissociates into a linear superposition of hydrogen atoms and positive and negative hydrogen ions, a completely unphysical result. This explains in part why the curve of total energy against interatomic distance for the valence bond method lies above the curve for the molecular orbital method at all distances and most particularly so for large distances. This situation arises for all homonuclear diatomic molecules and is particularly a problem for F2, where the minimum energy of the curve with molecular orbital theory is still higher in energy than the energy of two F atoms.

The concepts of hybridization are so versatile, and the variability in bonding in most organic compounds is so modest, that valence bond theory remains an integral part of the vocabulary of organic chemistry. However, the work of Friedrich Hund, Robert Mulliken, and Gerhard Herzberg showed that molecular orbital theory provided a more appropriate description of the spectroscopic, ionization and magnetic properties of molecules. The deficiencies of valence bond theory became apparent when hypervalent molecules (*e.g.* PF5) were explained without the use of d orbitals that were crucial to the bonding hybridisation scheme proposed for such molecules by Pauling. Metal complexes and electron deficient compounds (*e.g.* diborane) also appeared to be well described by molecular orbital theory, although valence bond descriptions have been made.

In the 1930s the two methods strongly competed until it was realised that they are both approximations to a better theory. If we take the simple valence bond structure and mix in all possible covalent and ionic structures arising from a particular set of atomic orbitals, we reach what is called the full configuration interaction wave function. If we take the simple molecular orbital description of the ground state and combine that function with the functions describing all possible excited states using unoccupied orbitals arising from the same set of atomic orbitals, we also reach the full configuration interaction wavefunction. It can be then seen that the simple molecular orbital approach gives too much weight to the ionic structures, while the simple valence bond approach gives too little. This can also be described as saying that the molecular orbital approach is too delocalised, while the valence bond approach is too localised.

The two approaches are now regarded as complementary, each providing its own insights into the problem of chemical bonding. Modern calculations in quantum chemistry usually start from (but ultimately go far beyond) a molecular orbital rather than a valence bond approach, not because of any intrinsic superiority in the former but rather because the

MO approach is more readily adapted to numerical computations. However better valence bond programmes are now available.

BONDS IN CHEMICAL FORMULAS

The 3-dimensionality of atoms and molecules makes it difficult to use a single technique for indicating orbitals and bonds. In molecular formulas the chemical bonds (binding orbitals) between atoms are indicated by various different methods according to the type of discussion. Sometimes, they are completely neglected. For example, in organic chemistry chemists are sometimes concerned only with the functional groups of the molecule. Thus, the molecular formula of ethanol (a compound in alcoholic beverages) may be written in a paper in conformational, 3-dimensional, full 2-dimensional (indicating every bond with no 3-dimensional directions), compressed 2-dimensional (CH3–CH2–OH), separating the functional group from another part of the molecule (C2H5OH), or by its atomic constituents (C2H6O), according to what is discussed.

Sometimes, even the non-bonding valence shell electrons (with the 2-dimensionalized approximate directions) are marked, *i.e.* for elemental carbon,'C'. Some chemists may also mark the respective orbitals, *i.e.* the hypothetical ethene”4 anion (\/C=C/\ “4) indicating the possibility of bond formation.

STRONG CHEMICAL BONDS

These chemical bonds are intramolecular forces, which hold atoms together in molecules. In the simplistic localized view of bonding, the number of electrons participating in a bond (or located in a bonding orbital) is typically multiples of two, four, or six, respectively. Even numbers are common because electrons enjoy lower energy states, if paired. Substantially more advanced bonding theories have shown that bond strength is not always a whole number, depending on the distribution of electrons to each atom involved in a bond.

For example, the carbons in benzene are connected to each other with about 1.5 bonds, and the two atoms in nitric oxide NO, are connected with about 2.5 bonds. Quadruple bonds are also well known. The type of strong bond depends on the difference in electronegativity and the distribution of the electron orbital paths available to the atoms that are bonded. The larger the difference in electronegativity, the more an electron is attracted to a particular atom involved in the bond, and the more “ionic” properties the bond is said to have (“ionic” means the bond electrons are unequally shared). The smaller the difference in electronegativity, the more covalent properties (full sharing) the bond has.

Molecular Mass Spectrometry

Mass spectrometry provides a powerful analytical tool for probing molecules for their bonding structure. Mass spectrometers are instruments that fragment and ionize "parent" molecules with electron beams and analyse the products with electric and magnetic fields and detectors. According to the laws of electromagnetism, charged particles passing through electromagnetic fields follow trajectories determined by their mass to charge ratio.

Thus fragments with different masses and/or different charges are separated by the external fields, except in the case where the mass to charge ratio happens to be the same. *E.g.* O+ (m/q = 16/1) will be distinguished from O2+ (m/q = 32/1) but not from O2+ 2 (m/q = 32/2 = 16/1). Relative amounts of parents and fragments measured by the detector reflect relative abundances in the sample. Mass spectra patterns give clues to the bonding of molecules. The first direct evidence that hydrogen is diatomic came in the early 1920's from a mass spectrometric analysis that showed two lines in the mass spectrum of elemental hydrogen, one with twice the mass as the other. More complicated molecules can have more complicated mass spectra, and computers are used to assist in the analysis. Complicating features include multiple combinations of possible "daughter" fragments, multiple ionizations of the parent and fragments, and multiple isotopes. If the molecules have a chance to react before analysis, fragments can recombine in new ways to confuse the analysis. A good way to analyse or predict a mass spectrum tabulates the possible combinations of parent and fragment masses, using isotope distributions to determine the spectral lines.

ATOMIC STRUCTURE AND BONDING

Atoms are composed of electrons, protons, and neutrons. Electron and protons are negative and positive charges of the same magnitude, 1.6 × 10-19 Coulombs. The mass of the electron is negligible with respect to those of the proton and the neutron, which form the nucleus of the atom. The unit of mass is an atomic mass unit (amu) = 1.66 × 10-27 kg, and equals 1/12 the mass of a carbon atom. The Carbon nucleus has Z=6, and A=6, where Z is the number of protons, and A the number of neutrons. Neutrons and protons have very similar masses, roughly equal to 1 amu. A neutral atom has the same number of electrons and protons, Z.

A mole is the amount of matter that has a mass in grams equal to the atomic mass in amu of the atoms. Thus, a mole of carbon has a mass of 12 grams. The number of atoms in a mole is called the Avogadro number, Nav = 6.023 × 1023. Note that Nav = 1 gram/1 amu.

Calculating n, the number of atoms per cm^3 in a piece of material of density (g/cm^3).

$$n = Nav \times / M$$

where M is the atomic mass in amu (grams per mol). Thus, for graphite (carbon) with a density ? = 1.8 g/cm3, M =12, we get 6 × 1023 atoms/mol × 1.8 g/cm3/ 12 g/mol) = 9 × 1022 C/cm3. For a molecular solid like ice, one uses the molecular mass, M(H2O) = 18. With a density of 1 g/cm3, one obtains n = 3.3 × 1022 H2O/cm3. Note that since the water molecule contains 3 atoms, this is equivalent to 9.9 × 1022 atoms/cm3.

Most solids have atomic densities around 6 × 1022 atoms/cm3. The cube root of that number gives the number of atoms per centimeter, about 39 million. The mean distance between atoms is the inverse of that, or 0.25 nm. This is an important number that gives the scale of atomic structures in solids.

Electrons in Atoms

The forces in the atom are repulsions between electrons and attraction between electrons and protons. The neutrons play no significant role. Thus, Z is what characterizes the atom. The electrons form a cloud around the neutron, of radius of 0.05 – 2 nanometers. Electrons do not move in circular orbits, as in popular drawings, but in 'fuzzy' orbits. We cannot tell how it moves, but only say what is the probability of finding it at some distance from the nucleus. According to quantum mechanics, only certain orbits are allowed (thus, the idea of a mini planetary system is not correct). The orbits are identified by a principal quantum number n, which can be related to the size, n = 0 is the smallest; n = 1, 2. are larger. (They are "quantized" or discrete, being specified by integers). The angular momentum l is quantized, and so is the projection in a specific direction m. The structure of the atom is determined by the Pauli exclusion principle, only two electrons can be placed in an orbit with a given n, l, m – one for each spin. Table 2.1 in the textbook gives the number of electrons in each shell (given by n) and subshells (given by l).

THE PERIODIC TABLE

Elements are categorized by placing them in the periodic table. Elements in a column share similar properties. The noble gases have closed shells, and so they do not gain or lose electrons near another atom. Alkalis can easily lose an electron and become a closed shell; halogens can easily gain one to form a negative ion, again with a closed shell. The propensity to form closed shells occurs in molecules, when they share electrons to close a molecular shell. Examples are H2, N2, and NaCl. The ability to gain or lose electrons is termed electronegativity or electropositivity, an important factor in ionic bonds.

BONDING FORCES AND ENERGIES

The Coulomb forces are simple: Attractive between electrons and nuclei, repulsive between electrons and between nuclei. The force between atoms is given by a sum of all the individual forces, and the fact that the electrons are located outside the atom and the nucleus in the center.

When two atoms come very close, the force between them is always repulsive, because the electrons stay outside and the nuclei repel each other. Unless both atoms are ions of the same charge (*e.g.*, both negative) the forces between atoms is always attractive at large internuclear distances r. Since the force is repulsive at small r, and attractive at small r, there is a distance at which the force is zero. This is the equilibrium distance at which the atoms prefer to stay.

The interaction energy is the potential energy between the atoms. It is negative if the atoms are bound and positive if they can move away from each other. The interaction energy is the integral of the force over the separation distance, so these two quantities are directly related. The interaction energy is a minimum at the equilibrium position. This value of the energy is called the bond energy, and is the energy needed to separate completely to infinity (the work that needs to be done to overcome the attractive force.) The strongest the bond energy, the hardest is to move the atoms, for instance the hardest it is to melt the solid, or to evaporate its atoms.

PRIMARY INTERATOMIC BONDS

Ionic Bonding

This is the bond when one of the atoms is negative (has an extra electron) and another is positive (has lost an electron). Then there is a strong, direct Coulomb attraction. An example is NaCl. In the molecule, there are more electrons around Cl, forming Cl- and less around Na, forming Na+. Ionic bonds are the strongest bonds. In real solids, ionic bonding is usually combined with covalent bonding. In this case, the fractional ionic bonding is defined as %ionic = 100 × [1 – exp(-0.25 (XA – XB)2], where XA and XB are the electronegativities of the two atoms, A and B, forming the molecule.

The Electronic Theory of Chemical Bonding

Nowadays it is recognized that the chemical bond is the most basic and essential feature of molecules. Understanding the properties of the interatomic bonds in molecules is essential to understanding the physical structure and chemical reactivities of molecular matter. Chemical bonds result from the electrostatic (Coulombic) interactions of the electrons and nuclei of atoms. Basically, the outer-shell electrons on each atom in a molecule can be thought to be attracted to the nuclei of adjacent atoms as well as their own nuclei. Fig. 12.2 diagrams the electrostatic interactions for a classical particle model of the dihydrogen molecule, the simplest neutral polyatomic molecule. Actually this model, although useful, is an oversimplification on several counts; as was found for atoms, electrons in the presence of nuclei do not behave as particles and classical models fall short of accurate descriptions of electronic structure.

The wave mechanical model of electronic structure is the appropriate description for multiple electron systems, and applies to molecules as well as atoms. The nature of the chemical bond is revealed in the solutions to Schr”odinger’s equation for molecules. As in the case of atoms, accurate solutions obtained for simple molecules are used to justify established bonding heuristics, as well as generate new molecular bonding principles. A major feature that emerges in investigating chemical bonds through wave mechanics is electrons prefer to be paired. This fact explains the stability of the simplest neutral molecule, H2 (with 2 paired electrons) with respect to H atoms, as well as the instability of He2 with respect to He atoms (each having 2 paired electrons). The stability of paired electrons and filled subshell electronic configurations prove to be most useful general principles for explaining a variety of features of molecules. Before delving further into the nature of the chemical bond as elucidated by the wave mechanics, we will explore a widely used powerful pre-wave mechanical bonding heuristic invented by G. N. Lewis3 early in the beginning of the Twentieth Century. Lewis considered electrons to be classical particles, which he represented graphically by dots.

Pairs of electrons between atoms he represented with lines to represent bonds connecting the atoms together. Lewis's contribution consisted of a simple method of counting the dots to predict chemical formulas, molecular geometry, and various chemical properties. By the beginning of the Twentieth Century, the sub-atomic structure of atoms was established and the stage was set for considering atomic attractions between atoms in terms of the interactive forces of the negatively-charged electrons and the positively-charged protons of the nucleus. In 1902 G. N. Lewis began using formulas of chemical compounds with little dots representing the electrons of the atoms in his lectures, which was the beginning of the electronic theory of chemical bonding. As Lewis searched for a theory to explain valency in terms of the electrons of an atom, he was led to the periodic table. We now know that columns of chemical families have similar properties because they have similar outer-shell electronic configurations, but that knowledge wasn't available at the beginning of the century.

Lewis reasoned that families of elements have similar properties because they have similar numbers of electrons participating in the bonding. This led to dividing the electrons of an atom into two categories, now known as inner shell, or core electrons and outer shell or valence electrons. There may be multiple inner shells of electrons, but the outer shell valence electrons are the ones closest to neighboring nuclei and therefore dominate in the chemical bonding. A chemically stable (inert) noble gas is found at the end of each row of the periodic table. The fact that each new noble gas has added at least eight more electrons, suggests some connection between eight electrons and stability. Atoms to the left and right of the noble gases have fewer than eight electrons, are less stable, and are hence chemically reactive. Lewis devised the octet rule to describe the tendency of atoms to gain stability by achieving an octet of outer shell, or valence electrons. However, there are exceptions. Elements in the first three columns of the periodic table may form suboctets (less than 8 electrons) and elements beyond the second row of the periodic table can form superoctets (more than 8 electrons).

Hydrogen is a notable exception, requiring merely a duet or pair of electrons to acquire the stability of the noble gas helium. The duet/octet heuristic, or "rule" states that atoms like to be noble (or have noble gas electronic configurations), or, in modern terms, filled subshells in electronic configurations are particularly stable. The octet heuristic was successful in describing the bonding in both ionic compounds (containing charged atoms or molecules) and covalent molecules (combinations of non-charged atoms) in terms of the valence electrons of atoms. In addition, the stability of paired electrons for the first time offered a rationalization4 of the stability of homonuclear diatomic gases, such as dihydrogen and dioxygen.

LEWIS STRUCTURES

Covalent pairs of electrons Lewis called bond pairs. Atoms with valence greater than unity could possibly share more than one pair of electrons with a neighbouring atom, producing stronger multiple bonds.5 Electrons left over after all the valences of the atoms were satisfied, Lewis classified as lone pair electrons. The identification of different classes of electrons in molecules proved very powerful in explaining their structures and reactivities. Molecular formulas which show the bonding and free electrons are called Lewis structure formulas. Lewis structures based on the duet/octet heuristic provide a simplified basis for explaining the properties of molecules.

ELECTRON CORRELATIONS IN SOLIDS

The variety of phenomena associated with the electronic structure of crystalline matter has been the subject of theoretical investigation for a long time. Historically, the starting impetus was given by the challenge of accounting for some peculiar properties of the metallic state, such as the excellent heat and electric conductivity. The quantum theory of electrons moving in a periodic lattice developed in the 1920's by Sommerfeld, Bloch, Wilson and others, for example, was indeed primarily aimed at understanding the electronic transport properties of metals. This theory led to the band model of the crystalline solid. It was realised that within the band model the configuration of the valence electrons can explain the division of perfect crystals at low temperatures into metals and insulators. If the valence electrons exactly fill one or more energy bands, leaving others empty, the crystal is an insulator. The difference in energy between the top of the highest occupied band and the bottom of the lowest empty band is known as the band gap. In the other case, when partially filled bands exist, the solid has metallic properties.

The band description of solids rests, as the simple orbital theories of atoms and molecules, on the independent electron approximation. Each electron experiences the periodic field due to the atomic nuclei and an effective field obtained by averaging over the positions of the remaining electrons. In spite of this approximation band theory has been very successful in predicting and understanding the properties of real materials, including elemental metals and many (simple) covalent and ionic compounds. It has been noticed, however, already in the 1930's that for some solids the one-electron band theory is inadequate. These are systems where, due to the competition between delocalization, band-like, effects and strong (atomic-like) electron – electron interactions, the independent electron approximation breaks down. Typical examples are the 3d -metal compounds.

In these compounds strong repulsive interactions may result in electron localization and the opening of a conductivity gap even though the d-"bands"are not completely filled. The presence of bound, unpaired, 3d electrons further gives rise to local magnetic moments and very rich magnetic properties. Serious attempts to characterize and understand the electronic structure of such materials began in the late 1950's. The main motivations at the time came from the issue of the Mott metal – insulator transition, the problem of magnetic ordering, and the problem of itinerant ferromagnetism. More recently, phenomena like heavy fermion behaviour, high-temperature superconductivity, colossal magnetoresistance, and spin-Peierls phase transitions have revived interest in these systems.

Nevertheless, although considerable effort has been put into the field, many of the transition metal materials are poorly understood.

The proper treatment of various competing physical effects, like electron localization as a result of strong electron – electron interactions and band-like behaviour as a result of orbital overlap and translational symmetry, remains one of the most difficult problems in theoretical solid state physics.

Wave-function based correlated quantum chemical methods have been successfully applied for calculating molecular electronic structures. A very attractive feature of the quantum chemical approach is the ability to address the electron correlation problem in a systematic and controlled manner. However, due to the high computational cost of these methods, inclusion of electron correlation effects in the study of crystalline solids did not seem feasible for a long time. Algorithms able to treat electron correlation explicitly in extended periodic systems have been developed only recently, either within the many-body second-order perturbation theory (MBPT2) or within the configuration interaction (CI) formalism. Still, calculations have been carried out for rather simple closed-shell systems only, like crystalline LiH and polymers.

Currently the most widely used first-principles method in solid state applications is the density functional (DF) theory within the local density approximation (LDA) (for a review). In the DF formalism, one avoids construction of the many-body wave-function and instead computes specific properties of the system from the ground-state electronic charge density. Recently, the study of the electronic response to external perturbations made possible calculation of low-energy excitations such as phonon dispersions, optical spectra and magnon dispersions. The DF-based methods approximately include electron correlation and usually give accurate estimates for a number of physical properties — calculated crystal structures, lattice parameters, elastic constants, dielectric functions and phonon frequencies are within a few per cent of the experimental values. Notable exception is the underestimation of the band gap. For strongly correlated 3d -electron systems like CoO and La2CuO4, DF/LDA calculations fail actually in predicting the correct insulating ground-state.

A different approach to the problem of strongly interacting electrons in solids is the model Hamiltonian method, where many-body effects are incorporated in some parameterized form. Two of the simplest models are the Hubbard

Hamiltonian widely used in a qualitative or a semi-quantitative way for studying the interplay between electron delocalization and electron repulsion effects, and the Anderson model of a magnetic impurity coupled to a conduction band. Model Hamiltonian investigations can often describe tendencies and reveal the basic mechanisms of various physical phenomena.

At the same time the model Hamiltonian approach is rather limited in its ability to make quantitative predictions, since even the simple Hubbard model can be solved exactly only in the one-dimensional case. In dealing with the two- and three-dimensional models numerical techniques are usually employed, based on quantum Monte Carlo methods or on diagonalizing the Hamiltonian for a cluster of atoms. However, the quantum Monte Carlo methods suffer from the so-called sign problem, while the exact diagonalization is limited by the exponential growth of the computational effort with the cluster size.

Local cluster (or atomic) impurity-like models have been used to describe various electronic properties of strongly correlated 3d- and 4f-metal systems for a long time, in combination with model Hamiltonians or with wave-function based quantum chemical calculations. Within the ab initio wave-function based approach the cluster is embedded in some effective potential that accounts for the crystal Madelung field and for short-range Pauli and exchange interactions due to the finite charge distribution of the nearest neighbours, respectively. The cluster contains one or more metal ions and the adjacent ligands. Proper treatment of the many-body problem, by configuration interaction techniques or second-order perturbation theory gives in several insulating transition metal materials accurate estimates and predictions for properties like core level spectra d – d excitations ligand to metal charge transfer effects and Heisenberg spin interactions.

In the study of the local many-body physics in solids a step forward consists in solving the problem of a (single- or multi-site) quantum impurity embedded in an effective medium self-consistently. This is the essential idea behind the dynamical mean field theory (DMFT), developed during the last decade (for a review). The DMFT reduces a lattice model to an Anderson impurity subject to a self-consistently determined "hybridization" with an electron "bath" representing the crystalline host. Its structure is that of a closed set of equations relating the "correlated"single-site impurity Green function to the crystal Green function evaluated at the impurity site. The crystal Green function can be calculated using standard DF/LDA band structure methods. Within such a LDA+DMFT scheme the DMFT correction to the LDA input results in a change of the electronic charge density. This updated charge density is used in a new LDA+DMFT loop and the cycle is repeated until convergence is reached. Results of such calculations were able, for example, to describe the finite-temperature magnetic properties of iron and nickel and the phase diagram of plutonium. Efforts to extend the single-site DMFT to include multi-site, short-range correlations led to the dynamical cluster approximation (DCA) and the cellular dynamical field theory (CDMFT).

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 IN CRYSTALS

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 $K = m_1b_1 + m_2b_2 + m_3b_3$ 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 neighbouring reciprocal lattice vectors. The consequences of periodicity are described mathematically by the Bloch wavefunction:

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

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 Schrφdinger equation Ø is well approximated by a linear combination of atomic orbitals $\psi n(r)$.

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

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 Schrφdinger solution for the n-th energy band as:

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

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 Methods and the ab Initio GW Approximation

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 $\Sigma = GW$ 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.

ENERGY BANDS

The electronic conductivity of a material is determined by the properties of its constituent atoms or molecules, and by the manner in which they are arranged in the lattice. A solid-state model that relates electronic processes to valance and conduction energy bands. The valance band consists of electrons that, because they have relatively low energy, are associated with individual atoms or molecules: the conduction band contains more energetic electrons that are free to move throughout the material in response to applied electromagnetic energy. The number and mobility of conduction electrons determines the electronic conductivity of a material. If the valance and conduction bands are separated by a small gap, then, at typical temperatures, thermal activity will deplete the valance band and populate the conduction band; such a material is a conductor. If the bands are widely separated in energy, the conduction band will be vacant and the material will be an insulator. A semiconductor is a material whose band structure falls between that of a conductor and an insulator-it can be an insulator at one temperature and a conductor at a higher temperature. Semiconductors can contain impurity atoms whose energy states lie within the gap between the valance and conduction bands; such impurities strongly affect conductivity by donating or accepting electrons.

An important consequence of the existence of energy bands is that they permit electronic processes in one region of a material to affect not only the immediate area, but also the entire structure. Szent-Gyorgyi proposed that common energy levels existed over relatively large dimensions in biological structures, possibly with the cell wall itself as the boundary. Evans and Gergely calculated the band gap in hydrogen-bonded models of biopolymers and showed that it would be so large that the biopolymers would behave electrically as insulators.

However, if impurity atoms were present, they could donate an electron to the conduction band, or remove one from the valance band, leading to mobile conduction electrons or mobile "holes" in the valance band. Szent-Gyorgyi postulated that these electronic processes within the energy bands-electron mobility in the conduction band and charge transfer in the valance band-could give rise to biological phenomena and, indeed, to life itself.

For ordinary materials the question of their band structure could be resolved by a coordinated series of X-ray, chemical, and electrondynamics studies. But biological tissue is inhomogeneous and impure, and suitable techniques for carrying out many of the necessary studies on such materials have not yet been developed. Perhaps the most significant problem for the experimentalist is that posed by the universal presence of water in tissue. It is well established that the electrical conductivity of tissue increases sharply with water content. However, the nature of electrical conduction in tissue under physiological conditions of temperature and moisture-the relative contribution of electronic, protonic, and ionic processes-has not been established despite more than 30 years of study.

Thus, no clear picture of the band structure in tissue has emerged. Other important solid-state techniques that have been used to study the electronic property of biological tissue include electron paramagnetic resonance, and photoconductivity. Again, although the results are consistent with a common-energy-band model proposed by Szent-Gyorgyi, they do not establish it as correct.

3

Solid-state Chemistry and Crystal Structure of Cefaclor Dihydrate

INTRODUCTION

Among the most exciting tools for the analytical chemist and biochemist are the modern spectrographs which are capable of providing structural as well as compositional information about compounds. While Emission spectroscopy is able to give accurate information as to the type of atoms present in a sample, it cannot give clues to the environment in which each kind of atoms exists. Less energetic methods are required for this purpose so that the integrity of molecules is maintained.

Three principal methods of modern spectrographic analysis are to be examined in this experiment: Mass Spectroscopy, Nuclear Magnetic Resonance, and Infra-Red Spectroscopy. Separately, each gives some information about a substance. Used in concert, they allow the positive identification of many, if not most, organic chemicals. In addition, preliminary classification of many organic compounds is possible through relatively simple qualitative tests similar in scope to those used to identify ions in The Separation and Analysis of a Mixture.

Organic compounds are *hydrocarbons*, *i.e.*, they contain at least hydrogen and carbon—often other elements such as nitrogen, oxygen, halogens, phosphorus and sulfur. Most of the bonding involved in organic compounds is covalent. The thermal stability of the compounds is thus less than that of similar molecular mass inorganic compounds. This is one reason less energetic means are used to study their structure.

The physical and chemical properties of organic compounds are highly structure-related. Attachment of small groups of atoms known as *functional groups* to a hydrocarbon can yield a new substance with properties—at least in part—characteristic of that group. Qualitative tests are capable of detecting the presence of such groups. Some common functional groups are listed on the following page for your reference.

THE QUALITATIVE TESTS

Alcohols are hydrocarbons with -OH replacing one or more hydrogen atoms. Alcohols have physical properties intermediate between those of hydrocarbons and water. Depending on where the -OH group appears, alcohols are classified as *primary* [on a carbon attached to only one other carbon], *secondary* [on a carbon attached to two other carbons], or *tertiary* [on a carbon attached to three other carbons]. Each type of alcohol reacts differently with a strong acid such as hydrochloric acid. The possible product, an alkyl halide, has limited solubility:

$$ROH + HCl\ ,, \rightarrow RCl + H_2O$$

[in this reaction as in most general organic reactions, *R* represents any hydrocarbon group]

This fact is used to advantage in the *Lucas test* in which an alcohol is combined with $ZnCl_2$ and HCl. The formation of the corresponding chloride (analogous to the formation of a chloride salt of a base) results in the separation of the mixture into two layers at varying rates. Tertiary alcohols react almost immediately. Secondary alcohols typically take from 5 to 10 minutes, becoming cloudy before separation occurs. Primary alcohols react very slowly (hours) or not at all.

However, the Lucas test can give many false indications and should not be accepted as foolproof. A study in 1991 by Kjonaas and Riedford pointed out that alcohols which are not sufficiently soluble in the reagent could be mistaken for tertiary or secondary alcohols. They suggested a follow-up test to confirm tertiary alcohols using concentrated HCl only.

Tertiary alcohols can be expected to react within 5 minutes whereas secondary and primary alcohols will not react. The test also often fails with secondary alcohols. The authors noted that temperature is important. They suggested 20-25°C. Also, using more alcohol than called for can lead to very long test times. Finally, mixing too much is not better. Swirling vigorously for 3 to 5 seconds and then allowing the mixture to stand appears to give the best results.

They added that test times are often longer if the reagent is added to the alcohol rather than the other way around. Aldehydes and ketones can undergo a variety of reactions, but they share many chemical properties with other related compounds such as acids and esters. It is possible to detect uniquely the presence of an aldehyde or ketone by reaction with 2,4-dinitrophenylhydrazine: [The orange crystalline product is often recovered and used to identify the compound because it has a well-defined (and generally published) melting point. But the formation of the orange crystals is enough to determine that one of these two compound types is present.

Aldehydes can be further screened out by their ease of oxidation. With $MnO_4{}^-$ aldehydes are oxidized to the corresponding acid and the MnO_4^- is reduced to brown insoluble MnO_2:

$$RCHO + MnO_4^- \rightarrow RCHOH + MnO_2 \text{ [not balanced]}$$

The *Baeyer test* for unsaturation also uses permanganate as an oxidizing agent, so some confusion may result if the test with 2,4-dinitrophenylhydrazine is not done first. Carboxylic acids react readily with sodium hydrogen carbonate, $NaHCO_3$, releasing carbon dioxide gas:

$$RCOOH + HCO_3^- \rightarrow RCOO^- + CO_2 + H_2O$$

Smaller acids also have a characteristic sour smell, not unlike that of acetic acid (ethanoic acid).

Amines (organic bases) are more difficult to distinguish by chemical tests, but most have a characteristic unpleasant smell which is associated with decomposing animal matter. However since amines and acids are soluble in water to some extent, it is often possible to identify them by the pH of a water solution. Acids will have pH values considerably less than 7 while amines will have values greater than 7. This will generally only work with smaller acids and amines, those having 5 or fewer carbons. Esters are most often identified by their “fruity” odors but some are rather unpleasant smelling, so this is no sure guide. Esters react with hydroxylamine hydrochloride to yield a compound which can complex with Fe^{3+} to give a coloured species:

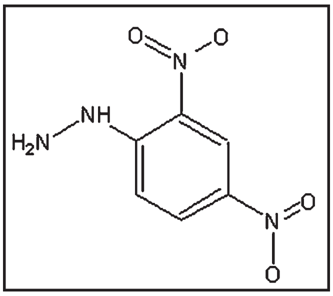
All carboxylic acid esters give magenta colours, which vary in intensity depending on structural features in the molecule. Because other types of compounds may also give “positive” tests, a preliminary screening test is generally used to help eliminate false positives. Compounds, which fail to give some kind of positive test indication with the above, may fall into the category of simple hydrocarbon (either aliphatic or aromatic), primary alcohol or some other less common type of compound. The only other simple test that can be done on your unknown would be an instauration test. To prevent this test from causing misinterpretation of an aldehyde, bromine addition is used instead of the oxidation with potassium permanganate. Compounds with double or triple bonds add bromine readily: The test is conducted by adding a small amount of the unknown to a solution of bromine in a non-polar and largely inert solvent (generally CCl_4). Addition of bromine and reduction of bond order is accompanied by rapid decolorization. This completes a background discussion of the qualitative organic tests for those common compounds containing functional groups.

EXPERIMENTAL TECHNIQUES

Both molecular spectroscopy and computational chemistry have witnessed rapid significant progresses in recent years. On the one hand, it is nowadays possible to compute, to quite a reasonable degree of accuracy, almost all fundamental spectroscopic properties for small molecular systems. The theoretical approach is now properly considered to be of fundamental importance in attaining a high degree of understanding of spectroscopic information. Moreover, it may be also a great help in designing and planning experiments. On the other hand, new and very powerful experimental techniques have been developed.

THE CHEMICALS

- *2,4-dinitrophenylhydrazine:* (2,4-DNPH), $C_6H_3(NO_2)_2NHNH_2$, is a red, crystalline powder that is slightly soluble in water and soluble in dilute inorganic acids. It is used for the determination of aldehydes and ketones and for the preparation of their derivatives. The solution used for these tests is tenacious with skin and contact should be avoided. Gloves are *strongly* recommended when using 2,4-DNPH. The dry solid is a suspected mutagen.



- *Potassium permanganate:* Consists of dark purple or bronze-like crystals and is a strong oxidizing agent. It is used extensively in laboratory work and also in dyeing wood, bleaching, photography, and tanning. Dilute solutions are mildly irritating to the skin and high concentrations are caustic. Potassium permanganate stains skin and clothing like silver nitrate.
- *Hydroxylamine hydrochloride:* (HH), $NH_2OH{\cdot}HCl$, consists of white crystals which slowly decompose when moist. The solid is fairly soluble in water, less so in ethanol and methanol. It is used as a reducing

agent in photography and as an antioxidant for fatty acids and soaps. It may be irritating to the skin, eyes and mucous membranes.

- *Iron(III) chloride:* Is a very hygroscopic reddish to yellow-brown solid generally found as the hexahydrate. It is readily soluble in water and acetone. The pH of 0.1 M solutions is 2.0. It is used in photoengraving, manufacture of other iron salts, inks, dyes and as a catalyst in organic reactions. Medically it has also been used as a topical astringent and styptic as well as in a test for phenylketonuria.
- *Sodium hydroxide:* Is commonly known as lye or caustic soda. It is a very hygroscopic white solid (absorbs water from the air rapidly) and also absorbs CO_2. It is very corrosive to vegetable and animal matter and aluminum metal, especially in the presence of moisture. Dissolving NaOH in water generates considerable heat. Besides its use in the laboratory, sodium hydroxide is used in commercial drain cleaner preparations, to treat cellulose in the manufacture of rayon and cellophane and in the manufacture of some soaps. It is corrosive to all tissues and can be detected on skin by the “slimy” feeling associated with bases. It should be rinsed off thoroughly upon contact. It can damage delicate eye tissues and cause blindness.

- *Hydrochloric acid:* Is also known as muriatic acid. It is the same liquid acid that is often used in controlling the pH of swimming pool water. It is sometimes coloured yellow by iron impurities, traces of chlorine and organic matter. Reagent grade HCl contains about 38% hydrogen chloride gas, close to the limit of its solubility at room temperature.

Hydrochloric acid in concentrated form (12 M) has the sharp, choking odour of hydrogen chloride. It is used in the production of other chlorides and in refining some ores (tin and tantalum), cleaning metal products, removing scale from boilers and heat-exchange equipment, and as an important laboratory reagent (often in diluted form). Concentrated solutions cause severe burns; permanent visual damage may occur. Inhalation causes coughing, choking; inflammation and ulceration of the respiratory tract may occur.

Ingestion can be fatal:

- *Zinc chloride (used in the Lucas Reagent)*: Is white, odorless, very deliquescent and highly soluble in water. The aqueous solution is acid to litmus (pH 4). It is used as a deodorant, for disinfectiing and enbalming and in the manufacture of parchment papers. It has also been used in a presevative for anatomical specimens. It is moderately irritating to the skin.
- *Dichloromethane*: CH_2Cl_2, is a colourless liquid. The vapour is not flammable. It is soluble in about 50

parts water and miscible with ethanol. Used as a solvent for cellulose acetate and for degreasing, the liquid has been used in the past as an inhalation anesthetic. It is narcotic in high concentrations.

- *Bromine (used in a solution of dichloromethane):* Is a dark reddish-brown fuming liquid at room temperature, consisting of diatomic molecules. In dilute water and hexane solutions its colour varies from golden to dark orange. In basic solutions at room temperature it slowly reacts to form bromide and hypobromous ions. It is a member of the halogen family and has a chemistry similar to chlorine. It attacks all metals and organic tissues and vaporizes readily at room temperature. Fumes are highly irritating to eyes and lungs.

  Bromine is used for bleaching silk, disinfecting spas, and manufacturing anti-knock compounds. Pure liquid bromine on the skin can cause painful, serious burns which heal only slowly.
- *2-propanone (commonly known as acetone)*: Is a volatile, highly flammable liquid with a characteristic odour and sweet taste. It is completely miscible with water, forming a low boiling azeotrope which speeds evaporation and drying (hence its frequent use in rinsing wet glassware and washing precipitates). It will attack many plastics including some synthetic fabrics

such as rayon. 2-propanone is used as a solvent for fats, oils, resins, waxes, lacquers, and rubber cements. It is also used in paint and varnish removers (some formulations of fingernail polish remover contain acetone). Prolonged or repeated topical exposure may cause skin dryness. Inhalation may produce headache, fatigue, and in large amounts, narcosis. Serious poisoning is rare.

- *The unknowns*: For obvious reasons, cannot be listed here in detail. They have been chosen for their *relatively* low toxicity and hazard. Some have moderately high vapour pressures and unpleasant odors. All should be treated with caution and skin contact should be avoided. Waste solutions from qualitative tests should be deposited into a container in the fume hood, not flushed down the sink. Residual material in test tubes or beakers should be removed with a rinse of a small amount of methanol. The rinsings should be added to the waste container.
- *Technique*: You will be provided with a small sample (approximately 15 mL) of an unknown organic liquid. You are to determine its identity by instrumental, physical and chemical means.

In general, the parts of the experiment may be done in any order, depending on the availability of instruments.

The logical approach set out below is only a guideline:

- The organic qualitative tests can be used to narrow down the type of compound.
- The HP 5890 GC/5970 Mass Spectrometer can be used to obtain the molar mass and fragmentation pattern.
- The Beynon programme will make it possible to determine the likely molecular formula of the compound.
- An NMR spectrum, using the EM-360 NMR Spectrometer, should be used for structural information.
- An IR spectrum, using the Perkin-Elmer 1420 IR Spectrometer, may be used to confirm functional groups and other structural details.
- Physical tests should be done to provide corroborative data. Two of the following are required:
  - Boiling point [in some cases this will exceed the range of our thermometers]
  - Density
  - Index of refraction

The qualitative tests that follow will help you to distinguish among the following types of compounds: ketones, aldehydes, esters, and different alcohols (1°, 2°, 3°). In addition to the series of tests outlined above, you should keep in mind that *hydrocarbons of less than 5 carbons are generally water soluble.* Carboxylic acids vary in solubility but their solutions will generally give a distinctly “acid” reading with pH paper. Unsaturation (as in alkenes or alkynes) can easily be detected by the immediate decolorization of added bromine. Some bromine dissolved in CH_2Cl_2 will be available for you to use.

Several types of compounds are not mentioned at all. These include the simple hydrocarbons (no functional group, either aliphatic or aromatic), ethers, halides, nitriles, nitro-compounds, etc. For the purposes of this experiment you may assume that any compound which tests *negative* for all of the tests given may fall into one of these categories *or may be a primary alcohol.*

Finally, it may be helpful to remember that most common aromatic compounds are benzene-based. Benzene is C_6H_6. Any substitutions on the benzene ring may raise the hydrogen:carbon ratio, but it is still lower than what would be expected in aliphatic compounds. Look for this characteristic in your likely molecular formulas. It can save you a lot of time. A more detailed description of the qual test scheme follows. remember, these substances should all be considered toxic. The less you use, the less there is to discard. Follow the directions closely as to the amounts of materials. More is not better.

Generic “knowns” are available for each test:

- *2,4-dinitrophenylhydrazine (2,4-DNPH) test*: To about 5 drops of 2,4-DNPH add a drop or two of your unknown. Ketones and aldehydes react immediately, forming unmistakable bright orange precipitates.

- *$KMnO_4$ test*: If the 2,4-DNPH test is positive, add 1 drop of the $KMnO_4$ solution to about 5 drops of your unknown. Aldehydes are readily oxidized to form brown precipitates. Ketones do not react.
- *Hydroxylamine hydrochloride (HH) test*: If the 2,4-DNPH test was negative, mix 1 mL of ethanol and 1-2 drops of the unknown; add 1 mL of 1 M HCl. Note the colour produced when 1 drop of 5% $FeCl_3$ is added. If the colour is orange, red, blue or violet, the following test will *not* yield valid results and should not be done. Mix 1-2 drops of the unknown, 1 mL of HH and 0.2 mL of 6 M NaOH. Heat to boiling [CAUTION!! it boils almost immediately and the mixture is flammable!!], cool slightly and add 2 mL of 1 M HCl. If the mixture is cloudy, add more (about 2 mL) ethanol. Add 1 drop 5% $FeCl_3$ and observe the colour. If the colour is burgundy or magenta as compared to yellow in the preliminary screening test, an ester is probably present.
- *Lucas test*: If all other tests have proven negative, you may have a simple hydrocarbon, acid, amine or alcohol. Place 10 drops of Lucas reagent in a small test tube. Add one drop of your unknown and swirl vigorously for 3-5 seconds. Allow to stand without further mixing. Tertiary alcohols (3^o) react immediately to form a cloudy solution. Secondary alcohols (2^o) take

from 5 seconds to 5 minutes to form a cloudy solution. Primary alcohols do not react. Be sure to review the background information about the Lucas test given in the introductory remarks. [2-propanol reacts in about 15 minutes using this method]

If all of these tests are negative, you may have an acid or amine which *may* be detected by adding a small amount of the compound to water and testing the mixture with pH paper. Simple unsaturated hydrocarbons are best detected by the Br_2 addition test. However, the presence of other unsaturations (such as carbonyls) can give confusing results. Generally, alkenes react *immediately* while other groups react more slowly. To do this test add 2 drops of your unknown to two drops of the Br_2/CH_2Cl_2 mixture and swirl to mix. Rapid decolorization indicates the presence of –C=C–.

FRANCK – CONDON PRINCIPLE

The Franck-Condon principle states that after a molecule is excited from its ground electronic state the nuclear conformation must readjust. This leads to, in general, an increase in the “allowed” vibronic transitions and hence greatly influences the observed spectrum. For all but the simplest models for the electronic potentials, one must resort to a numerical calculation of the observed spectrum. However if we are able to determine the functional form for the wave functions of more complicated models, we can utilize the analytic capabilities of *Mathematic* to calculate the (Franck-Condon) spectrum.

There are a number of interesting models which are simple enough to determine the wave functions yet to complicate to work out the theoretical spectra by hand. This project also has application to the vibration spectra of molecules in the condensed phase. This project will give you experience with and important topic in physical chemistry and also with *Mathematic*.

Franck–Condon principle is the approximation that an electronic transition is most likely to occur without changes in the positions of the nuclei in the molecular entity and its environment. The resulting state is called a Franck–Condon state, and the transition involved, a vertical transition. The quantum mechanical formulation of this principle is that the intensity of a vibronic transition is proportional to the square of the overlap integral between the vibrational wavefunctions of the two states that are involved in the transition.

PRINCIPLE

Radiative electronic transitions (mainly dipolar) in the molecule occur very fast with respect to the re-adjustment time of the inter-atomic distance (R). Then, in spite of similar radial dependence of the potential energy curves for different electronic levels, these curves are shifted with respect to one another in function of the excitation energy.

So, The R values corresponding to a high probability of presence of the electron in the Saa state (first index correspond to the electronic energy state, second index to the vibrationnal energy level) correspond to a low probability of presence for the Sia state $(j \neq 0)$, As the transition probability is proportional to the square of the overlap integral between wave functions, transitions between states of same vibrationnal quantum number is highly unprobable. So, during excitation, a π electron in Saa the state will be excited to aSij $(j \neq 0)$ and the absorbed energy (SE_{exc}) will be larger than the energy difference (SE) between the two energy Saa levels and Sia. After excitation, the electron will rapidly *fall down* to the first vibrationnal level by non-radiative transitions. after that, the radiative de-excitation will take place between the Sia state to the Saj' state. $(j \neq 0)$ the emitted energy (SE_{aci}) will then be lower than SE.

Finally:

$$SE_{aci} < SE < SE_{exc}$$

The difference between SE_{exc} and SE_{aci} explains the shift between emission and absorption spectra of a molecule and is called the *Stokes shift*.

Franck-Condon considerations

The Frank-Condon principle states that electronic transitions take place in times that are very short compared to the time required for the nuclei to move significantly. Because of this, care must be taken to ensure that the calculations actually do reflect what is wanted.

Examples of various phenomena which can be studied are:

- *Photoexcitation*: If the purpose of a calculation is to predict the energy of photoexcitation, then the ground-state should first be optimized. Once this is done, then a C.I. calculation can be carried out using 1SCF. With the appropriate keywords (MECI C.I.=*n* etc.), the energy of photoexcitation to the various states can be predicted. A more expensive, but more rigorous, calculation would be to optimize the geometry using all the C.I. keywords. This is unlikely to change the results significantly, however.
- *Fluorescence*: If the excited state has a sufficiently long lifetime, so that the geometry can relax, then if the system returns to the ground state by emission of a photon, the energy of the emitted photon will be less (it will be red-shifted) than that of the exciting photon.

  To do such a calculation, proceed as follows:
  - Optimize the ground-state geometry using all the keywords for the later steps, but specify the ground state, *e.g.* MECI C.I.=3 GNORM=0.01 .
  - Optimize the excited state, *e.g.* C.I.=3ROOT=2 GNORM=0.01 MECI.
  - Calculate the Franck-Condon excitation energy, using the results of the ground-state calculation only.
  - Calculate the Franck-Condon emission energy, using the results of the excited state calculation only.

  - If indirect emission energies are wanted, these can be obtained from the DH_f of the optimized excited and optimized ground-state calculations.

  In order for fluorescence to occur, the photoemission probability must be quite large, so only transitions of the same spin are allowed. For example, if the ground state is S_0, then the fluorescing state would be S_1.

- *Phosphorescence*: If the photoemission probability is very low, then the lifetime of the excited state can be very long (sometimes minutes). Such states can become populated by S T_1 intersystem crossing. Of course, the geometry of the system will relax before the photoemission occurs.
- *Indirect emission*: If the system relaxes from the excited electronic, ground vibrational state to the ground electronic, ground vibrational state, then a more complicated calculation is called for.

  The steps of such a calculation are:
  - Optimize the geometry of the excited state.
  - Using the same keywords, except that the ground state is specified, optimize the geometry of the ground state.
  - Take the difference in DH_f of the optimized excited and optimized ground-state calculations.
  - Convert this difference into the appropriate units.
- *Excimers*: An excimer is a pair of molecules, one of which is in an electronic excited state. Such systems are usually stabilized relative to the isolated systems.

Optimization of the geometries of such systems is difficult.

MAGNETIC RESONANCE

Magnetic Resonance (MR), which has no known biological hazard, is capable of producing high resolution thin tomographic images in any plane and blocks of 3-dimensional information. It can be used to study blood flow and to gain information about the composition of important materials seen and quantified on dimensionally accurate images.

The MR image is a thin tomography slice or a true three dimensional block of data which can be reconstructed in any desired way rather than a shadow gram of all the structures in the beam. It is the only imaging technique which can acquire data in a 3-dimensional format. CT images can be reconstructed to form a pseudo 3-D image or a hologram but the flexibility conferred by acquiring the data as a true 3-D block gives many advantages.

The spatial resolution of MR images are theoretically those of low powered microscopy, the practical limits with the present generation of equipment are voxel sizes of one third by one third by two millimeters.

The term Magnetic Resonance Imaging (MRI) is used commonly, particularly in the USA, avoiding association with the term, nuclear, and emphasizing the imaging potential of the technique. The terms Nuclear Magnetic Resonance (NMR) or Magnetic Resonance (MR) more correctly describe the most powerful diagnostic instrument yet devised. The simplified description of the phenomena involved in MR which follows is intended to be comprehensive and does not require foreknowledge of classical physics, quantum mechanics, fluency with mathematical formulae or an understanding of image reconstruction.

Magnetic resonance spectroscopy can be used to extract *in vivo* biochemical information from body tissue. Like the more familiar magnetic resonance imaging (MRI) it is based on the principle that atomic nuclei within molecules behave like tiny magnets in the presence of an externally applied magnetic field and resonate at a characteristic frequency. MRS techniques have been used in *in vitro* biochemistry for many years but have only recently been employed in the study of biochemical changes in different organs of the living human body. Although still a relatively new technique, MRS has been used in the study of numerous psychiatric disorders and has already yielded interesting results that may help to bridge the gap between clinical observation and neuroscience. The aims of this paper are to provide a basic and brief overview of the principles and technology of MRS and to summaries the major findings reported in psychiatric disorders.

BASIC PRINCIPLES

Atomic nuclei with odd numbers of protons or neutrons behave like magnetic dipoles and rotate around an axis, like the Earth around its axis. The alignment of this axis is random. However, when atomic nuclei are placed in a powerful external magnetic field they tend to align along the direction of this field. When a second magnetic field is applied in the form of a brief pulse they absorb the extra energy and temporarily shift the orientation of their alignment. When the pulse is removed, they return to their original alignment and emit electromagnetic energy inducing a voltage signal. This signal can then be mathematically processed using Fourier transformation to yield the magnetic resonance spectrum.

Another concept basic to the understanding and interpretation of MRS findings is that of chemical shift. The rotation of atomic nuclei around their axis occurs at a frequency which is unique for each nucleus. This is called the Larmor frequency and is affected by the local magnetic fields surrounding a given nucleus. These local magnetic fields are generated by the electrons surrounding the nucleus. If these fields were absent, all the nuclei of a given atom would resonate at exactly the same frequency when placed in a homogeneous magnetic field. This would yield a single signal in the form of a sharp peak. However, because of the variation in local magnetic fields, the same nucleus in different molecules resonates at subtly different frequencies resulting in divergence from a single peak and giving rise to a spectrum. Chemical shift is the term used to describe this phenomenon of peak dispersion and allows for the discrimination, identification and quantification of different molecules.

When magnetically active molecules are placed in an external magnetic field they align themselves along the direction of the field and demonstrate a circular oscillation. The frequency of this circular motion (called Larmor frequency) is dependent on the strength of the local magnetic field and the structure of these molecules. When electromagnetic energy (in the form of a radiofrequency, or

RF, pulse) is supplied at this frequency, the molecules absorb this energy and change their alignment. When the external energy is switched off, the molecules realign themselves to the magnetic field by releasing their absorbed energy. This released energy is the basis of the MR signal.

Local magnetic fields are dependent on the externally applied magnetic field, the localization gradients applied, and the locally present molecules. The first two factors being constant, the change in the Larmor frequency induced by the locally present molecules may be calculated by detecting the changing MR parameters such as free induction decay (FID), T2 time, T1 time, etc., in response to the applied RF pulse. This change in the local Larmor frequency is used to calculate the amount of any particular molecule within the sample volume. These changes are, however, very small and therefore difficult to detect accurately. Virtually any nucleus can be interrogated using this technique; however, the two most widely used nuclei are phosphorus (31P) as it is a marker of energy metabolism, and hydrogen (1H) as it is the most magnetically active particle in the human body. Hydrogen-based MR spectroscopy, which is also called proton MR spectroscopy, is now the most widely used and its application in neuroimaging.

Technique

MRS can be performed by two methods - single-voxel spectroscopy (SVS), where a single sample volume is selected and a spectrum obtained from it, or multi-voxel spectroscopy where spectra are obtained from multiple voxels in a single slab of tissue. SVS gives a better signal-tonoise ratio and is a more robust technique. The disadvantage is that only a single spectrum is obtained. The placement of the volume of interest (VOI) becomes critical3 and may lead to errors of interpretation if not done correctly. With multivoxel MRS, a much larger area can be covered, eliminating the sampling error to an extent. This is however done at the expense of a significant weakening in the signal-to-noise ratio and a longer scan time. Both SVS and multi-voxel imaging utilize specialized MR pulse sequences.

INFORMATION IN NMR

IDEA

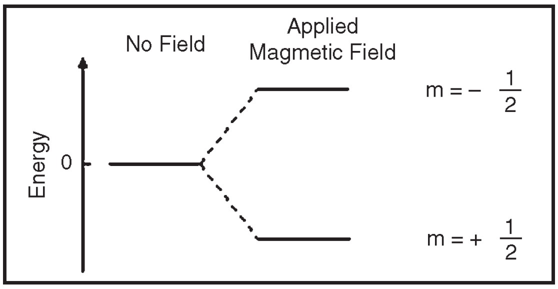
Over the past fifty years nuclear magnetic resonance spectroscopy, commonly referred to as nmr, has become the preeminent technique for determining the structure of organic compounds. Of all the spectroscopic methods, it is the only one for which a complete analysis and interpretation of the entire spectrum is normally expected. Although larger amounts of sample are needed than for mass spectroscopy, nmr is non-destructive, and with modern instruments good data may be obtained from samples weighing less than a milligram. To be successful in using nmr as an analytical tool, it is necessary to understand the physical principles on which the methods are based.

The nuclei of many elemental isotopes have a characteristic spin (I). Some nuclei have integral spins (*e.g.* $I = 1, 2, 3....$), some have fractional spins (*e.g.* $I = 1/2, 3/2, 5/2....$), and a few have no spin, $I = 0$ (*e.g.* ^{12}C, ^{16}O, ^{32}S....). Isotopes of particular interest and use to organic chemists are ^{1}H, ^{13}C, ^{19}F and ^{31}P, all of which have $I = 1/2$. Since the analysis of this spin state is fairly straightforeward, our discussion of nmr will be limited to these and other $I = 1/2$ nuclei. Subatomic particles (electrons, protons and neutrons) can be imagined as spinning on their axes. In many atoms (such as ^{12}C) these spins are paired against each other, such that the nucleus of the atom has no overall spin. However, in some atoms (such as ^{1}H and ^{13}C) the nucleus does possess an overall spin.

The rules for determining the net spin of a nucleus are as follows:

- If the number of neutrons and the number of protons are both even, then the nucleus has NO spin.
- If the number of neutrons plus the number of protons is odd, then the nucleus has a half-integer spin (*i.e.* 1/2, 3/2, 5/2)
- If the number of neutrons and the number of protons are both odd, then the nucleus has an integer spin (*i.e.* 1, 2, 3)

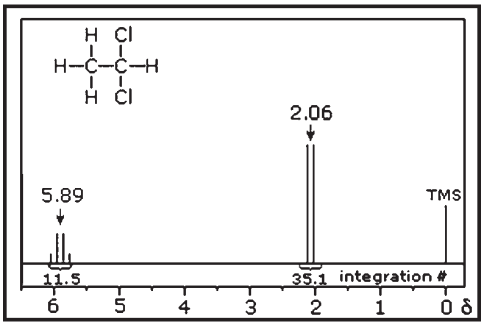
The overall spin, I, is important. Quantum mechanics tells us that a nucleus of spin I will have $2I + 1$ possible orientations. A nucleus with spin 1/2 will have 2 possible orientations. In the absence of an external magnetic field, these orientations are of equal energy. If a magnetic field is applied, then the energy levels split. Each level is given a magnetic quantum number, m.



When the nucleus is in a magnetic field, the initial populations of the energy levels are determined by thermodynamics, as described by the Boltzmann distribution. This is very important, and it means that the lower energy level will contain slightly more nuclei than the higher level. It is possible to excite these nuclei into the higher level with electromagnetic radiation. The frequency of radiation needed is determined by the difference in energy between the energy levels.

SPIN-SPIN COUPLING

The spin-spin interaction of neighbouring hydrogens takes place through the covalent bonds that join them. The most common bonding relationship is vicinal (joined by three sigma bonds). In this case a neighbouring proton having a +1/2 spin shifts the resonance frequency of the proton being observed to a slightly higher value (up to 7 Hz), and a –1/2 neighbouring spin shifts it to a lower frequency. Remember that the total population of these two spin states is roughly equal, differing by only a few parts per million in a strong magnetic field. If several neighbouring spins are present, their effect is additive.



In the spectrum of 1,1-dichloroethane shown in figure 7.2, it is clear that the three methyl hydrogens (red) are coupled with the single methyne hydrogen (orange) in a manner that causes the former to appear as a doublet and the latter as a quartet. The light gray arrow points to the unperturbed chemical shift location for each proton set. By clicking on one of these signals, the spin relationship that leads to the coupling pattern will be displayed. Clicking elsewhere in the picture will return the original spectrum.

The statistical distribution of spins within each set explains both the n+1 rule and the relative intensities of the lines within a splitting pattern. The action of a single neighbouring proton is easily deduced from the fact that it must have one of two possible spins. Interaction of these two spin states with the nuclei under observation leads to a doublet located at the expected chemical shift. The corresponding action of the three protons of the methyl group requires a more detailed analysis. In the display of this interaction four possible arrays of their spins are shown.

The mixed spin states are three times as possible as the all +1/2 or all –1/2 collection. Consequently, we expect four signals, two above the chemical shift and two below it. This spin analysis also suggests that the intensity ratio of these signals will be 1:3:3:1. The line separations in splitting patterns are measured in Hz, and are characteristic of the efficiency of the spin interaction; they are referred to as coupling constants (symbol J). In the above example, the common coupling constant is 6.0 Hz.

A simple way of estimating the relative intensities of the lines in a first-order coupling pattern is shown on the right. This array of numbers is known as Pascal's triangle, and is easily extended to predict higher multiplicities. The number appearing at any given site is the sum of the numbers linked to it from above by the light blue lines. Thus, the central number of the five quintet values is 3 + 3 = 6. Of course, a complete analysis of the spin distributions, as shown for the case of 1,1-dichloroethane above, leads to the same relative intensities.

Coupling constants are independent of the external magnetic field, and reflect the unique spin interaction characteristics of coupled sets of nuclei in a specific structure. As noted earlier, coupling constants may vary from a fraction of a Hz to nearly 20 Hz, important factors being the nature and spatial orientation of the bonds joining the coupled nuclei. In simple, freely rotating alkane units such as CH_3CH_2X or YCH_2CH_2X the coupling constant reflects an average of all significant conformers, and usually lies in a range of 6 to 8 Hz. This conformational mobility may be restricted by incorporating the carbon atoms in a rigid ring, and in this way the influence of the dihedral orientation of the coupled hydrogens may be studied.

The inductive effect of chlorine shifts the resonance frequency of the red coloured hydrogen to a lower field (δ ca. 4.0), allowing it to be studied apart from the other hydrogens in the molecule. The preferred equatorial orientation of the large tert-butyl group holds the six-membered ring in the chair conformation depicted in the drawing. In the trans isomer this fixes the red hydrogen in an axial orientation; whereas for the cis isomer it is equatorial.

The listed values for the dihedral angles and the corresponding coupling constants suggest a relationship, which has been confirmed and clarified by numerous experiments.

SPIN-SPIN RELAXATION

Nuclei in an NMR experiment are in a sample. The sample in which the nuclei are held is called the *lattice*. Nuclei in the lattice are in vibrational and rotational motion, which creates a complex magnetic field. The magnetic field caused by motion of nuclei within the lattice is called the *lattice field*. This lattice field has many components. Some of these components will be equal in frequency and phase to the Larmor frequency of the nuclei of interest. These components of the lattice field can interact with nuclei in the higher energy state, and cause them to lose energy (returning to the lower state). The energy that a nucleus loses increases the amount of vibration and rotation within the lattice (resulting in a tiny rise in the temperature of the sample). The relaxation time, T_1 (the average lifetime of nuclei in the higher energy state) is dependant on the magnetogyric ratio of the nucleus and the mobility of the lattice. As mobility increases, the vibrational and rotational frequencies increase, making it more likely for a component of the lattice field to be able to interact with excited nuclei. However, at extremely high mobilities, the probability of a component of the lattice field being able to interact with excited nuclei decreases.

SPIN - SPIN RELAXATION

Spin - spin relaxation describes the interaction between neighbouring nuclei with identical precessional frequencies but differing magnetic quantum states. In this situation, the nuclei can exchange quantum states; a nucleus in the lower energy level will be excited, while the excited nucleus relaxes to the lower energy state. There is no net change in the populations of the energy states, but the average lifetime of a nucleus in the excited state will decrease. This can result in line-broadening.

Spin-Spin Relaxation time T_2(Transverse)

The existence of relaxation implies that an NMR line must have a width. The smallest width can be estimated from the uncertainty principle. Since the average lifetime of the upper state cannot exceed T_1, this energy level must be broadened to the extent: h/T_1. This means that line width at half-height of the NMR line must be at least: $1/T_1$.

In Solution NMR, very often T_2 and T_1 are equal (small/ medium molecules and fast tumbling rate). For solids, T_1 is usually much larger than T_2. The very fast spin-spin relaxation time provide very broad signals. There are other processes that can increase the line width substantially over the expected value extracted from T_1 analysis. T_2 represents the lifetime of the signal in the transverse plane (XY plane) and it is this relaxation time that is responsible for the line width. The “true” line width on an

NMR signal depends on the relaxation time T_2 (line width at half-height=$1/T_2$). In fact, by measuring the experimental line width, one can in principle determine the T_2 relaxation time. Unfortunately, the experimental line width depends also on the inhomogeneity from the magnetic field. The experimental relaxation rate, extracted from the line width, is called $1/T_2^*$ ($1/T_2^*=1/T_2 + 1/T_2$(inhomogeneity)). The inhomogeneity factor is more critical for nuclei with higher frequency (more critical for proton than for Carbon or Phosphorus). The reason behind this statement can be explained as follows: imagine that identical nuclei (identical chemical shift) in a NMR tube are submitted to slightly different field (inhomogeneity from the magnet). The resonance frequency for each individual nuclei is described by the equation: $\nu = \gamma B_0$. If the field vary through the NMR tube, so do the observed frequency, broadening the NMR line. This broadening would affect more the proton (higher γ) than lower frequency nuclei. The broadening is in fact directly proportional to the frequency.

Spin-Spin Relaxation Mechanisms

The same mechanisms that are active in Spin-Lattice are active for spin-spin relaxation. You can consult them on the T_1 description. We will describe here the mechanisms that can bring extra broadening to the peak.

Scalar relaxation occurs when two spins interact through bond (electron mediated) - J coupling.

Spin I can feel fluctuating in the field from spin S in two ways:

1. The scalar coupling J can be time dependent due to chemical exchange If nuclei S is jumping in and out of a site in which it is coupled to spin I, splitting will collapse at high rate. At intermediate rate, the line will broaden due to partial scalar coupling (this can be observed on exchangeable protons like OH or NH)
2. The spin S can be time dependent due to rapid relaxation of spin S (like in quadrupolar nuclei)

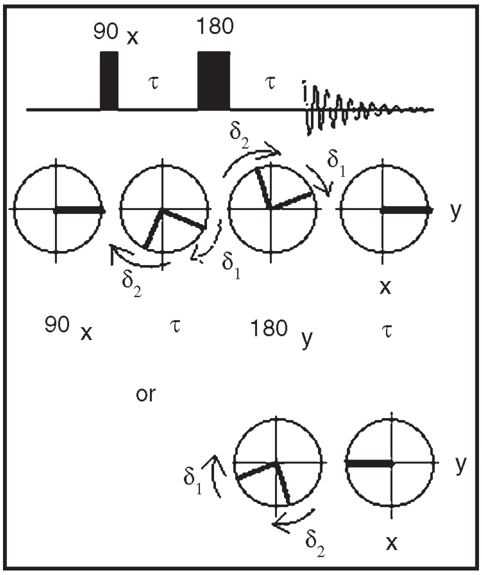
Relaxation Induced by Quadrupolar Nuclei

If the relaxation time of the quadrupolar nuclei is rapid ($1/T_1(S) >> 2*pi*J$), nuclei I will not couple to the quadrupolar nuclei. *e.g.* ^1H next to ^{14}N or ^{11}B (T_1 => 10-100 msec) => produce broadened lines *e.g.* ^1H next to ^{35}Cl (T_1 => 1 *u*sec) => insignificant broadening Scalar coupling with rapidly relaxing quadrupolar nucleus can be determined based on T_1 and T_2 analysis.

Measurement of T_2 Relaxation Process

In non-viscous liquids, usually $T_2 = T_1$. But some process like scalar coupling with quadrupolar nuclei, chemical exchange, interaction with a paramagnetic center, can accelerate the T_2 relaxation such that T_2 becomes shorter than T_1. In principle T_2 can be obtained by measuring the signal width at half-height (line-width = $(pi * T_2)^{-1}$

However the line width for non-viscous liquids is most often dominated by field inhomogeneity. Fortunately, the dephasing of spins isochromats resulting from field inhomogeneity is a reversible process: it can be refocused by using a 180 degree pulse inserted in the center of an evolution time.



- The Hahn echo is constituted first by a 90 degree pulse that flips the magnetization in the XY plane.
- During the first *tau* delay, the magnetization evolve according to it's chemical shift (and field inhomogeneity)
- Then a 180 pulse is applied. This 180 degree pulse inverts the magnetization. (This pulse can be applied along the X or the Y axis).
- Following the inversion pulse, another *tau* delay is applied. During this delay, the magnetization refocus:

  - for example, if the nuclei with chemical shift 1 have had the time to precess clockwise by 15 degree during the first *tau* delay, it will also precess by the same amount after the inversion pulse as the identity of the nuclei have not been changed.
  - Similarly, if field inhomogeneity is present for the first tau delay, the same inhomogeneity is present after the inversion pulse and will influence the precession in the same manner allowing us to refocus this unwanted effect at the end of the second delay.
  - This will give rise to an echo after the 2**tau* delays. The size of this echo will only be affected by the spin-spin relaxation processes.
- *At the end of the second delay, the echo will be lined up*:
  - Along the Y axis if the 180 degree pulse was applied along the Y axis,
  - Along the -Y axis if the 180 degree pulse was applied along the X axis.

The Carr-Purcell-Meiboom-Gill (CPMG) sequence shown above is derived from the Hahn spin-echo sequence. This sequence is equipped with a “built-in” procedure to self-correct pulse accuracy error. In the picture above, only the first shift is shown but with field inhomogeneity. The letters f and s means that those nuclei affected by the inhomogeneity of the magnet precess faster and slower than the chemical shift respectively.

- If the first inversion pulse applied is shorter (*e.g.* 175 degree) than a 180 degree pulse, a systematic error is introduced in the measurement. The echo will form above the XY plane (*e.g.* 5 degree) and therefore the signal will be smaller than expected.
- To correct that error, instead of sampling immed-iately the echo, a third *tau* delay is introduced, during which, the magnetization evolve as before but slightly above the XY plane (see figure above).
- If the second inversion pulse, also shorter than a 180 degree pulse (*e.g.* 175 degree), is applied, as the magnetization is already above the plane, this shorter inversion pulse will put the magnetization exactly in the XY plane.
- At the end of the last *tau* delay, the echo will form exactly in the XY plane self correcting the pulse error!

SPIN-LATTICE RELAXATION

For nmr spectroscopy to be practical, an efficient mechanism for nuclei in the higher energy –1/2 spin state to return to the lower energy +1/2 state must exist. In other words, the spin population imbalance existing at equilibrium must be restored if spectroscopic observations are to continue. Now an isolated spinning nucleus will not spontaneouly change its spin state in the absence of external perturbation. Indeed, hydrogen gas (H_2) exists as two stable spin isomers: ortho (parallel proton spins) and para (antiparallel spins). Nmr spectroscopy is normally carried out in a liquid phase (solution or neat) so that there is close contact of sample molecules with a rapidly shifting crowd of other molecules (Brownian motion). This thermal motion of atoms and molecules generates local fluctuating electromagnetic fields, having components that match the Larmor frequency of the nucleus being studied. These local fields stimulate emission/absorption events that establish spin equilibrium, the excess spin energy being detected as it is released.

This relaxation mechanism is called Spin-Lattice Relaxation (or Longitudinal Relaxation). The efficiency of spin-lattice relaxation depends on factors that influence molecular movement in the lattice, such as viscosity and temperature. The relaxation process is kinetically first order, and the reciprocal of the rate constant is a characteristic variable designated T_1, the spin-lattice relaxation time. In non-viscous liquids at room temperature T_1 ranges from 0.1 to20 sec. A larger T_1 indicates a slower or more inefficient spin relaxation. Another relaxation mechanism called spin-spin relaxation (or transverse relaxation) is characterized by a relaxation time T_2.

NUCLEAR OVERHAUSER EFFECT

The nuclear overhauser effect (or NOE) is a special case of nuclear relaxation in nuclear magnetic resonance (NMR) spectro-scopy and magnetic resonance imaging (MRI). The purpose of proton decoupling is to eliminate overlapping signal patterns and to increase the signal to noise ratio. Decoupling of the protons increases the signal to noise ratio by causing the collapse of quartets, triplets, and doublets to singlets and by causing a favourable increase in the number of carbons in the a-spin state relative to the -spin state. The latter effect is called the Nuclear Overhauser Effect (NOE) In a typical NMR or MRI experiment, a nucleus in a magnetic field absorbs photons of a frequency mostly determined by the elemental identity of the nucleus (*e.g.* hydrogen, carbon etc.) and the strength of the applied magnetic field (see Zeeman effect.) Nuclei so treated are said to be in an excited nuclear spin state, and they literally spin like a top in said magnetic field. They can be observed by the current their spinning generates in wire coils looped around the sample compartment, be it an NMR tube or the huge cavernous opening in an MRI device.

It is basically the transfer of spin polarization from one spin population to another is generally called Overhauser Effect, after American Physicist Albert Overhauser who hypothesized it in the early 1950s. It occurs under different conditions (*e.g.* between electrons and atomic nuclei) yet is most commonly observed and used amongst atomic nuclei and then named Nuclear Overhauser Effect (NOE). A very common application is NOESY (Nuclear Overhauser Effect

SpectroscopY), a Magnetic Resonance technique for structure determination of macromolecular motifs.

But they don't spin forever. One nucleus in an excited spin state can transfer its magnetization to another nucleus in a process called dipolar coupling. The rate at which this happens between a given pair of nuclei is inversely proportional to the cube of the distance between. It's also a complicated function of the angle between the line formed by the two atoms and the external magnetic field. Since most NMR experiments are performed in solution, and most MRI experiments involve observation of the protons on water molecules in a solution-like environment, this angle varies considerably during the time course of the experiment, as the molecules being observed are moving and spinning all over the place. This is called isotropic rotational averaging, and under these conditions the rate of magnetization transfer is independent of the angle between the magnetic field and the intern clear vector, but inversely proportional to the sixth power of the distance between them. Magnetization transfer by dipolar coupling under the conditions of isotropic rotational averaging is called the *nuclear overhauser effect.* This is the principal pathway by which any nucleus being observed in solution loses its magnetization, thus it is the main factor contributing to nuclear relaxation. Note that the magnitude of both the NOE and dipolar coupling are independent of the nature of the intervening medium, they are *through-space* interactions, as opposed to through-bond interactions like J-coupling.

This may seem pretty esoteric but in fact it forms the basis, along with J-coupling, for the determination ofprotein, DNA and RNA structures and their interactions with other molecules. One merely excites some particular nucleus, waits a period of time, and observes where the magnetization has been transferred. Because of the aforementioned distance dependence of the magnetization transfer, this allows the 3-dimensional mapping of the molecule when the experiment is repeated for a sufficient percentage of the nuclei in a molecule. The method of NMR has overtaken that of x- easily observe the interaction of these biomolecules with small molecule drug candidates. ray crystallography as the method of choice for rational drug design not because of its ability to determine structures, but because the nuclear overhauser effect allows one to quickly.

APPLICATIONS OF NMR

The scientific literature contains literally thousands of reports concerning fundamental and applied studies of NMR that implicate its use in determining properties and compositions of wide varieties of materials, both liquid and solid. The literature also contains numerious specific examples of the use of time-domain NMR for component analysis. In most cases, these techniques can be directly applied for other determinations wherein the physical and NMR properties of the samples are similar.

13*C* NMR

Carbon-13 NMR or ^{13}C NMR, sometimes referred to as carbon NMR is the application of nuclear magnetic resonance spectroscopy with respect to carbon. It is analogous to proton NMR (^{1}H NMR) and allows the identification of carbon atoms in an organic molecule just as proton NMR identifies hydrogen atoms. As such ^{13}C NMR is an important tool in chemical structure elucidation in organic chemistry. ^{13}C NMR detects only the ^{13}C isotope of carbon, whose natural abundance is only 1.1%, because the main carbon isotope, ^{12}C, is not detectable by NMR.

^{13}C NMR has a number of complications that are not encountered in proton NMR. ^{13}C NMR is much less sensitive to carbon than ^{1}H NMR is to hydrogen since the major isotope of carbon, the ^{12}C isotope, has a spin quantum number of zero and so is not magnetically active and therefore not detectable by NMR. Only the much less common ^{13}C isotope, present naturally at 1.1% natural abundance, is magnetically active with a spin quantum number of 1/2 (like ^{1}H) and therefore detectable by NMR. Therefore, only the few ^{13}C nuclei present resonate in the magnetic field, although this can be overcome by isotopic enrichment of eg. protein samples. In addition, the gyromagnetic ratio (6.728284 10^7rad T^{-1} s^{-1}) is only 1/4 that of ^{1}H, further reducing the sensitivity. The overall *receptivity* of ^{13}C is about 4 orders of magnitude lower than ^{1}H. Another potential complication results from the presence of large one bond J-coupling constants between carbon and hydrogen (typically from 100 to 250 Hz). In order to suppress these couplings, which would otherwise complicate the spectra and further reduce sensitivity, carbon NMR spectra are proton decoupled to remove the signal splitting. Couplings between carbons can be ignored due to the low natural abundance of^{13}C. Hence in contrast to typical proton NMR spectra which show multiplets for each proton position, carbon NMR spectra show a single peak for each chemically non-equivalent carbon atom.

In further contrast to ^{1}H NMR, the intensities of the signals are not normally proportional to the number of equivalent ^{13}C atoms and are instead strongly dependent on the number of surrounding spins (typically ^{1}H). Spectra can be made more quantitative if necessary by allowing sufficient time for the nuclei to relax between repeat scans. High field magnets with internal bores capable of accepting larger sample tubes, the use of relaxation reagents, for example Cr and appropriate pulse sequences have reduced the time needed to acquire quantitative spectra and have made quantitative carbon-13 NMR a commonly used technique in many industrial labs. Applications range from quantification of drug purity to determination of the composition of high molecular weight synthetic polymers. ^{13}C chemical shifts follow the same principles as those of ^{1}H, although the typical range of chemical shifts is much larger than for ^{1}H. The chemical shift reference standard for ^{13}C is the carbons in tetramethylsilane, whose chemical shift is considered to be 0.0 ppm.

Nuclear Magnetic Resonance (NMR) Spectroscopy is not limited to the study of protons. Any element with a nuclear spin (^{13}C, ^{17}O, ^{19}F,^{31}P and many others) will give rise to an NMR signal.

Carbon-13 has a nuclear spin ($I = ½$) and makes up 1.1% of all naturally occurring carbon, a high enough abundance along with modern technology to make carbon nuclear magnetic resonance spectroscopy (^{13}C-NMR) a useful technique. Since carbon is the element central to organic chemistry, ^{13}C-NMR plays an important role in determining the structure of unknown organic molecules and the study of organic reactions and processes.

The idea and theory behind ^{13}C-NMR is the same as with ^{1}H-NMR, just a different nucleus, so you really do not have to learn anything new to understand and interpret ^{13}C-NMR's to help you solve structures of unknown organic compounds.

In particular, the^{13}C-NMR spectrum of an organic compound provides information concerning:

- The # of different types of carbon atoms present in the molecule
- The electronic environment of the different types of carbons
- The number of “neighbours” a carbon has (splitting)

The major differences that you will notice in ^{13}*C-NMR in comparison to* ^{1}*H-NMR spectra include*:

- No integration of carbon spectra
- Wide range (0-200 ppm) of resonances for common carbon atoms (typical range for protons 1-10 ppm)

Use the index on the left to choose which topic you want to go. If you are pretty good at interpreting ^{13}C-NMR, you may want to go straight to the exercises. If not, maybe you could visit the tutorial pages and take the included quizzes.

4

Structures and Properties of Solids

OPTICAL PROPERTIES

A particle placed in a beam of light will scatter some of the light incident on it (*i.e.* the light will change direction) and absorb some of the light (*i.e.* the electromagnetic energy is transformed into other forms of energy by the particle). The light we then receive has been attenuated or, to put it another way, suffered extinction.

The amount of light scattered and/or absorbed by the particle depends, in an intricately involved way, on the exact nature of the particle, and also the nature of the incident light. Consequently the extinction is dependent on the chemical composition of the particle and its size, shape and orientation, together with the wavelength and polarization state of the light. Therefore, we must include all these factors in our interpretations of spectra.

Identification of astronomical dust is usually achieved by comparing the observed spectral data with a catalogue of laboratory spectra of materials considered to be similar to those found in the astronomical dust. A computer programme can be used to make correlations between the reference spectra and the observed spectra, however there are limitations to this technique. In order to compare the laboratory and observed spectra they need to be of similar type, *i.e.* transmission spectra of very fine particulate materials. Many of the available spectra are obtained from samples for which no attempt has been made to simulate the possible conditions in the observed astronomical dust. One of the reasons for this is that the laboratories want to optimize the surface conditions of the sample to yield the maximum amount of spectral information. Also, the applications to which infrared spectra are put are diverse and therefore the collection of such spectra uses many different techniques, producing different types of spectra, according to the application. A complete understanding of the transmission and reflection properties of both particulate and bulk media is imperative for the correct interpretation of the spectral data.

PHYSICAL OPTICS

Absorption, reflection, scattering, polarization and dispersion of light by a material medium can all be explained in terms of the atoms, molecules and lattice structures which make up the medium. This section will concentrate on the mechanisms by which electromagnetic radiation is absorbed by matter.Absorption of radiation by matter always involves the loss of energy by the radiation and a gain in energy by the atoms or molecules of the medium.

The energy of an assembly of atoms consists partly of thermal energy and partly of internal energy associated with the binding of the extra-nuclear electrons to the nucleus and with the binding of the particles within the nucleus itself. Molecules have, in addition, energy associated with the oscillations of the atoms within the molecule with respect to one another, and solids have energy associated with intermolecular bonds. The energy absorbed from radiation appears as increased internal energy or as increased vibrational energy of interatomic or intermolecular bonds.

Classical Electromagnetic Theory

In classical electromagnetic theory, atoms and molecules are considered to contain electrical charges (*i.e.* electrons, ions) which are regarded as oscillating about positions of equilibrium, each with its appropriate natural frequency, o, When placed in a radiation field of frequency , each oscillator in the atom or molecule is set into forced vibration with the same frequency as that of the radiation. If << o or >> o , the amplitude of the forced vibration is small, but as approaches the amplitude of the forced vibration increases rapidly. To account for the absorption of energy from the radiation field, it is necessary to assume that the oscillator in the atom or molecule must overcome some frictional force proportional to its velocity during its forced motion.

For small amplitudes of forced oscillation, when is very different from o , the frictional force, and therefore the absorption of energy, is negligible. Near resonance (i.e is approx. equal to o), the amplitude of oscillation becomes large, with a correspondingly large absorption of energy to overcome the frictional force. Therefore, the radiation of frequencies near the natural frequency of the oscillator corresponds to an absorption band.

Acoustic and Optical Modes

Now, let us examine the allowed vibration modes in a lattice. The most rudimentary lattice we can consider is a linear chain of identical atoms. If we displace the nth atom from its equilibrium position by a small amount ðn parallel to the chain, the neighbouring atoms ((n-1)th and (n+1)th) will also be displaced by,

ðn – ðn – 1 and ðn – ðn + 1 respectively. Therefore the nth atom is actually displaced by an amount ðn – ðn – 1 with respect to the (n-1th) atom, and by ðn – ðn + 1 with respect to the (ð + 1)th atom.

According to the Lorentz model, these atoms can be considered to be connected by springs. Therefore the n th atom will experience a restoring force F equivalent to that of

Hooke's Law. Because the n th atom is connected to two springs (one to each neighbouring atom) there will be two contributions to this force, which is given by:

$$F = -\eta\ [(\eth n - \eth n - 1) - (\eth n + 1 - \eth n)]$$

where η is the spring constant. Applying Newton's second law we also get:

$$F = m\ .\ d2\eth n/dt2$$

where m is the mass of the oscillator. Thus,

$$d2\eth n/dt2 = (\eta/m)\ [(\eth n - \eth n - 1) - (\eth n + 1 - \eth n)]$$

Solutions to equation have the form:

$$\eth n = \eth o\ \ ei(kna - \omega t)$$

where is the angular frequency of the wave, k is the wavenumber and ðo is the amplitude of oscillation.

If we now substitute equation we get:

$$\omega 2 = 2(\eta/m)\ [1\text{-}\cos(ka)]$$

$$\omega 2 = 4(\eta/m)\ \sin 2(ka/2)$$

$$\omega = \pm 2\ (\eta/m)\ \tfrac{1}{2}\sin(ka/2)$$

This equation gives the allowed vibration modes in this simple lattice. From equationit is obvious that $\omega > 2(\eta/m)\tfrac{1}{2}$ is not possible. Frequencies above $\omega = 2(\eta/m)\tfrac{1}{2}$ cannot propagate through the lattice. In this model the displacement of the oscillator is along the chain, therefore the wave motion is longitudinal. This is the longitudinal acoustic mode.

Now consider a chain in which there are two different atoms of type X and Y, with masses mX and mY respectively (mX > mY), placed alternately along the chain. Again we displace the nth atom, of type X, by a small amount ðn. The nearest neighbouring atoms, both of type Y, are displaced by ðn-1 and ðn+1 as before; the next nearest atoms, both of type X, are displaced by ðn-2 and ðn+2 and so on. We have two different atom types in the chain, so we require two equations for the restoring force: one for the nth atom of type X and one for the (n+1)th atom of type Y.

Hence we get:

$$FX = -\eta\ X[(ðn - ðn-1) - (ðn + 1 - ðn)]$$

$$FY = -\eta Y[(ðn - ðn+1) - (ðn+1 - ðn+2)]$$

For simplicity, let $\eta X = \eta Y = \eta$. Again we can use Newton's second law and get:

$$FX = mX\ .\ d2ðn/dt2$$

$$FY = mY\ .\ d2ðn+1/dt2$$

And again, analogous to the monatomic chain we get solutions of the form:

$$ðn = ðX\ \ ei(kna - \omega t)$$

$$ðn = ðY\ \ ei(k(n + 1)a - \omega t)$$

From which we get:

$$\omega 2 = \eta[(1/mX) + (1/mY)] \pm \eta[\{(1/mX) + (1/mY)\}2 - \{4\sin 2(ka)\}/mXmY]$$

If we take the negative sign in equation, we get the acoustic mode already encountered, with the maximum allowed frequency at = $2(\eta/mX)½$ again. However, if we take the positive sign in equation, we get the optical mode, so called because this mode is easily excited by radiation of the appropriate frequency in ionic solids. In this case we find that there is a range of permitted frequencies with both a maximum and a minimum which correspond to the longitudinal and transverse optical (LO and TO) modes.

The minimum frequency (TO) is given by:

$$\omega TO = 2(\eta/mY)^{1/2}$$

The maximum frequency (LO) is given by:

$$\omega LO = 2[\eta/\{(1/mX)+(1/mY)\}]^{1/2}$$

The transverse and longitudinal optical modes represent the onset and cutoff of an absorption band. It is generally thought that absorptivity measurements only involve the TO component, however, in reality the LO component can play an important role (Berreman 1963). The contribution from the LO mode depends on the constituents of the molecule/ solid under consideration as well as the crystal structure, grain size/sample thickness etc. The conditions under which the spectrum is taken and the nature of the spectrometer also affect the relative contributions from the TO and LO modes. It is therefore necessary to understand the contributions from all these factors in order to interpret spectra correctly.

ELECTRICAL PROPERTIES OF MATTER

At the beginning of this section the mechanism by which electromagnetic radiation loses energy to material media was outlined. We have just concluded a simple discussion of the permitted frequencies in a material medium. Now we need to combine these two: we have a system in which atoms or molecules are connected by “springs” and that are forced to oscillate in an electric field. The motion is affected by friction in the guise of a damping force. If the oscillator has mass m and charge q, we can expect an equation of motion of the form:

$$m\ (d2\eth/dt2) + b\ (d\ \eth/dt) + \eta\eth = qE$$

where $\eth$ is the displacement of the oscillator, b is the damping force, η is the spring constant and E electric field of the electromagnetic radiation incident on the material. The electric field is assumed to be time harmonic with frequency ω. From equation we can see that η is approximately equal to $m\ \omega\ o2$ (where ωo is the natural frequency of the medium); the damping force can be written as $b = \gamma m$, where γ is the damping coefficient.

Thus, equation becomes:

$$d2\eth/dt2 + \gamma(d\ \eth/dt) + \omega o2\eth = qE/m$$

The solution of equation is:

$$\eth = (-qE/m)\ .\ [1\ /\ \{(\omega o2 - \omega2\ ) - i\gamma\,\omega\}]$$

which gives us an induced dipole moment, p, of:

$$p = (-q2E/m).[1/\{(\omega o2 - \omega2\ ) - i\gamma\,\omega\}]$$

If we assume that the displacement $\eth$ is small we can also assume that there is a linear relationship between the induced dipole moment and the electric field, which gives:

$$p = a(\omega)E$$

where $a(\omega)$ is the frequency dependent polarizability of the atom or molecule. Combining equations:

$$a = (-q2/m)\ .\ [1/\{(\omega o2 - \omega 2) - i\gamma\,\omega\}]$$

Because of the inclusion of the damping term, the polarizability is a complex quantity. If there are N oscillators per unit volume, the macroscopic polarizability, P, is given by:

$$P = N < p > = N\,a\,E$$

From Maxwell's equations we can get a complex displacement, D, given by:

$$D = E = E + 4P$$

where is the complex dielectric function. Substituting for P from equation we get:

$$\begin{aligned} E &= E + 4N\ a\ E \\ &= 1 + 4N\ a \end{aligned}$$

now substituting from equation we get:

$$= 1 + (4N\ q2)/m.[1/\{(\omega o2 - \omega 2\ ) - i\gamma\,\omega\}]$$

The dielectric function is complex and can, therefore, be written as:

$$= \in' + \in''$$

From equation we get:

$$\in' = 1 + (4N\ q2)/m.[(\omega o2 - \omega 2\ )/\{(\omega o2 - \omega 2)2 + \gamma 2\ \omega 2\}]$$

$$\in'' = 1 + (4N\ q2)/m.[(\gamma\omega)/\{(\omega o2 - \omega 2\ )2 + \gamma 2\ \omega 2\}]$$

We have expressions for the real and imaginary parts of the complex dielectric function (and). What do these expressions tell us about the response of a material to electromagnetic radiation? Let us consider the frequency dependence of and, The frequency dependences given by equations which shows that, for most of the spectrum, increases with increasing frequency, This is known as normal dispersion. However, for a small section close to the resonance frequency of the oscillator, o, the value of decreases with increasing, This is known as anomalous dispersion. The width of the region of anomalous dispersion is determined by the strength of the damping coefficient,, For small values of , the region of anomalous dispersion is narrow.

However, for large values of , the anomalous dispersion covers a broader range of frequencies, and hence the region over which absorption by the medium extends is broader. Inspection of equations also shows us that, for small values of , the value of remains small and the peak of is very close to the resonance frequency of the medium, o. Likewise, has its anomalous region centred at about o. However, for large values of , the situation is quite different. With increasing , the height of the peak of becomes much larger and the peak position moves away from the resonance frequency, as does the position of the anomalous region in, Since is the measure of the damping within a medium, *i.e.* the mechanism by which the medium absorbs energy from electromagnetic radiation, large values of correspond to highly absorbing media. Similarly, low values of correspond to relatively transparent media. Therefore, for relatively non-absorbing materials, a region of anomalous dispersion, and therefore an absorption feature, coincides approximately with the resonance frequency of the oscillators. Furthermore, for highly opaque, absorbing materials, the anomalous dispersion and the absorption feature will be shifted away from the resonance frequency of the oscillators.

As can easily be seen from equation the physical property of a solid that determines its dielectric function is its electric polarizability, which, in turn, consists of contributions from the individual dipole moments of the oscillators within the solid. It is therefore useful to consider what actually constitutes these dipole moments.

There are three possible sources of individual dipole moments in solids to examine:

1. The dipole moments due to the orientation of polar molecules in the solid;
2. Ionic polarisation due to the relative movement of the ions in the solid;
3. Electronic polarisation due to the displacement of atomic electrons relative to the nuclei. Depending on the nature of the solid, the first two considerations may not be applicable (*i.e.* the solid may not contain polar molecules or ions), however all solids contain electrons and nuclei and therefore electronic polarisation is found in all solids. The contributions to the dielectric function from these three types of "oscillators" lead to features in three separate regions of the spectrum. The dipole moments of polar

molecules are expected to give rise to features in the ~1011Hz (~3mm) region of the spectrum; likewise the ionic polarisation affects the spectrum in the ~1013Hz (30μm) region (the infrared); and the electronic polarisation will make contributions at ~1015 (0.3μm; UV). Therefore we expect some solids to exhibit spectral features in all these regions.