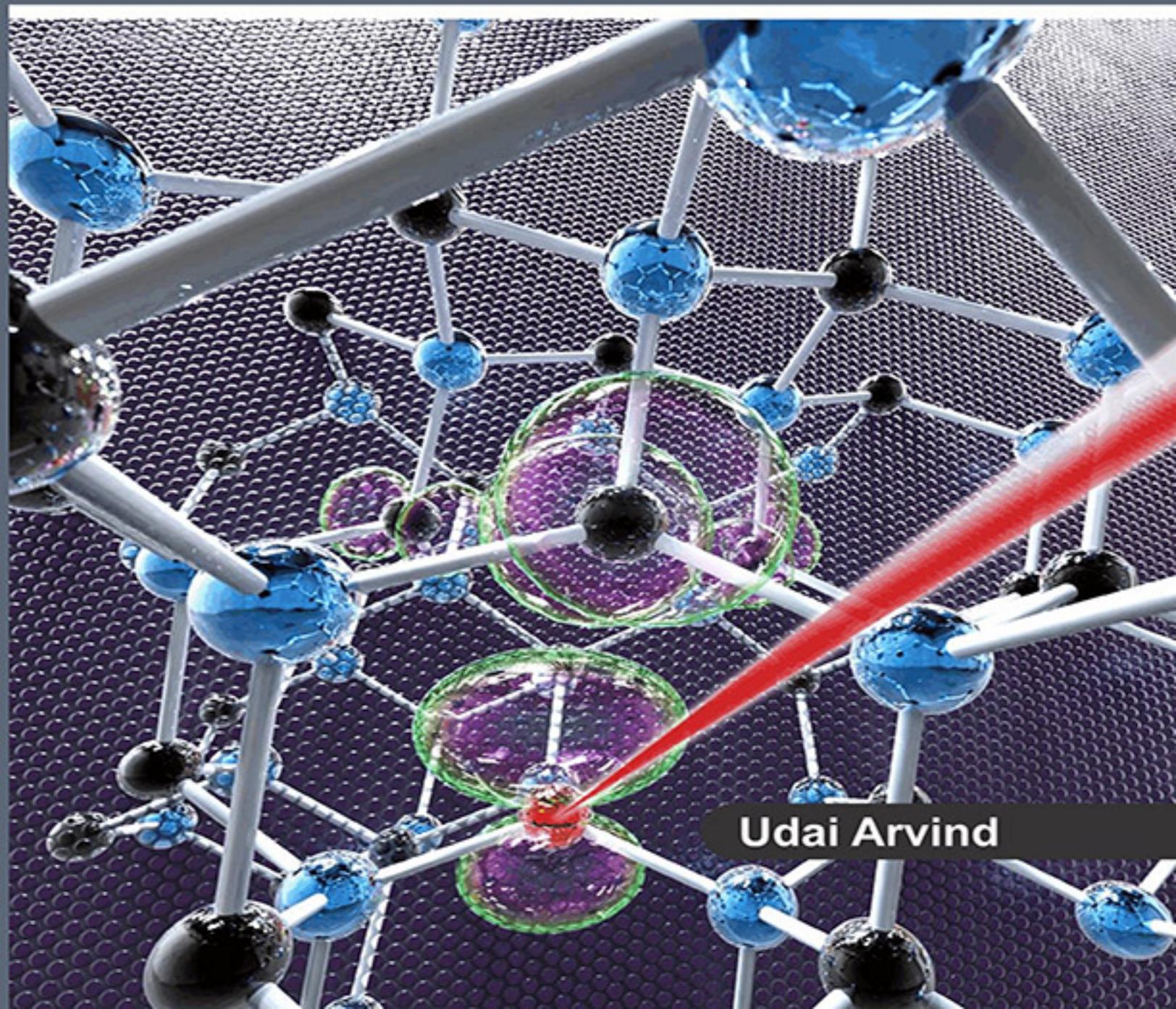


CONCEPTS IN

Solid State Chemistry



Udai Arvind

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SOLID STATE CHEMISTRY**

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Preface

Solid-state chemistry, also sometimes referred to as materials chemistry, is the study of the synthesis, structure, and properties of solid phase materials, particularly, but not necessarily exclusively of, non-molecular solids. It therefore has a strong overlap with solid-state physics, mineralogy, crystallography, ceramics, metallurgy, thermodynamics, materials science and electronics with a focus on the synthesis of novel materials and their characterization. Because of its direct relevance to products of commerce, solid state inorganic chemistry has been strongly driven by technology. Progress in the field has often been fuelled by the demands of industry, well ahead of purely academic curiosity. Applications discovered in the 20th century include zeolite and platinum-based catalysts for petroleum processing in the 1950s, high-purity silicon as a core component of microelectronic devices in the 1960s, and “high temperature” superconductivity in the 1980s. The invention of X-ray crystallography in the early 1900s by William Lawrence Bragg enabled further innovation. Our understanding of how reactions proceed at the atomic level in the solid state was advanced considerably by Carl Wagner’s work on oxidation rate theory, counter diffusion of ions, and defect chemistry. Because of this, he has sometimes been referred to as the *father of solid state chemistry*. Given the diversity of solid state compounds, an equally diverse array of methods are used for their preparation. For organic materials, such as charge transfer salts, the methods operate near room temperature and are often similar to the techniques of organic synthesis.

Redox reactions are sometimes conducted by electrocrystallisation, as illustrated by the preparation of the Bechgaard salts from tetrathiafulvalene. For thermally robust materials, high temperature methods are often employed. For example, bulk solids are prepared using tube furnaces, which allow reactions to be conducted up to ca. 1100 °C. Special equipment e.g. ovens consisting

of a tantalum tube through which an electric current is passed can be used for even higher temperatures up to 2000 °C. Such high temperatures are at times required to induce diffusion of the reactants, but this depends strongly on the system studied. Some solid state reactions already proceed at temperatures as low as 100 °C. One method often employed is to melt the reactants together and then later anneal the solidified melt. If volatile reactants are involved the reactants are often put in an ampoule that is evacuated -often while keeping the reactant mixture cold e.g. by keeping the bottom of the ampoule in liquid nitrogen- and then sealed. The sealed ampoule is then put in an oven and given a certain heat treatment. It is possible to use solvents to prepare solids by precipitation or by evaporation. At times the solvent is used hydrothermally, i.e. under pressure at temperatures higher than the normal boiling point. A variation on this theme is the use of flux methods, where a salt of relatively low melting point is added to the mixture to act as a high temperature solvent in which the desired reaction can take place. Many solids react readily with reactive gas species like chlorine, iodine, oxygen etc. Others form adducts with other gases, e.g. CO or ethylene. Such reactions are often carried out in a tube that is open ended on both sides and through which the gas is passed. A variation of this is to let the reaction take place inside a measuring device such as a TGA. In that case stoichiometric information can be obtained during the reaction, which helps identify the products. A special case of a gas reaction is a chemical transport reaction. These are often carried out in a sealed ampoule to with a small amount of a transport agent, e.g. iodine is added. The ampoule is then placed in a zone oven. This is essentially two tube ovens attached to each other which allows a temperature gradient to be imposed. Such a method can be used to obtain the product in the form of single crystals suitable for structure determination by X-ray diffraction. Chemical vapour deposition is a high temperature method that is widely employed for the preparation of coatings and semiconductors from molecular precursors.

The present book deals with all the important dimensions of this subject. It is a valuable reference source for all those concerned with this subject.

—Editor

1

Solids

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, ω_0 . When placed in a radiation field of frequency ω , each oscillator in the atom or molecule is set into forced vibration with the same frequency as that of the radiation. If $\omega \ll \omega_0$ or $\omega \gg \omega_0$, the amplitude of the forced vibration is small, but as ω approaches ω_0 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 ω is very different from ω_0 , the frictional force, and therefore the absorption of energy, is negligible. Near resonance (i.e. ω is approx. equal to ω_0), 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 n th atom from its equilibrium position by a small amount δ_n parallel to the chain, the neighbouring atoms ($(n-1)$ th and $(n+1)$ th) will also be displaced by,

δ_{n-1} and δ_{n+1} respectively. Therefore the n th atom is actually displaced by an amount $\delta_n - \delta_{n-1}$ with respect to the $(n-1)$ th atom, and by $\delta_n - \delta_{n+1}$ with respect to the $(n+1)$ 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:

$$F = -\eta [(\delta_n - \delta_{n-1}) - (\delta_{n+1} - \delta_n)]$$

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

$$F = m \cdot d^2\delta_n/dt^2$$

where m is the mass of the oscillator. Thus,

$$d^2\delta_n/dt^2 = (\eta/m) [(\delta_n - \delta_{n-1}) - (\delta_{n+1} - \delta_n)]$$

Solutions to equation have the form:

$$\delta_n = \delta_0 e^{i(kna - \omega t)}$$

where ω is the angular frequency of the wave, k is the wavenumber and δ_0 is the amplitude of oscillation.

If we now substitute equation we get:

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

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

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

This equation gives the allowed vibration modes in this simple lattice. From equation it is obvious that $\omega > 2(\eta/m)^{1/2}$ is not possible. Frequencies above $\omega = 2(\eta/m)^{1/2}$ 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 m_X and m_Y respectively ($m_X > m_Y$), placed alternately along the chain. Again we displace the n th atom, of type X, by a small amount δ_n . The nearest neighbouring atoms, both of type Y, are displaced by δ_{n-1} and δ_{n+1} as before; the next nearest atoms, both of type X, are displaced by δ_{n-2} and δ_{n+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 n th atom of type X and one for the $(n+1)$ th atom of type Y.

Hence we get:

$$F_X = -\eta X [(\delta_n - \delta_{n-1}) - (\delta_{n+1} - \delta_n)]$$

$$F_Y = -\eta Y [(\delta_n - \delta_{n+1}) - (\delta_{n+1} - \delta_{n+2})]$$

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

$$F_X = m_X \cdot d^2\delta_n/dt^2$$

$$F_Y = m_Y \cdot d^2\delta_{n+1}/dt^2$$

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

$$\delta_n = \delta_X e^{i(kna - \omega t)}$$

$$\delta_{n+1} = \delta_Y e^{i(k(n+1)a - \omega t)}$$

From which we get:

$$\omega^2 = \eta \left[\frac{1}{m_X} + \frac{1}{m_Y} \right] \pm \eta \left[\left(\frac{1}{m_X} + \frac{1}{m_Y} \right)^2 - 4 \sin^2(ka) \right]^{1/2}$$

If we take the negative sign in equation, we get the acoustic mode already encountered, with the maximum allowed frequency at $\omega = 2(\eta/m_X)^{1/2}$ 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:

$$m (d^2\delta/dt^2) + b (d\delta/dt) + \eta\delta = qE$$

where δ 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 $m \omega_0^2$ (where ω_0 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:

$$d^2\delta/dt^2 + \gamma(d\delta/dt) + \omega_0^2\delta = qE/m$$

The solution of equation is:

$$\delta = (-qE/m) \cdot [1 / \{(\omega_0^2 - \omega^2) - i\gamma\omega\}]$$

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

$$p = (-q^2E/m) \cdot [1 / \{(\omega_0^2 - \omega^2) - i\gamma\omega\}]$$

If we assume that the displacement δ 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:

$$a = (-q^2/m) \cdot [1 / \{(\omega_0^2 - \omega^2) - i\gamma\omega\}]$$

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:

$$P = N \langle p \rangle = N a E$$

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

$$D = \epsilon E = \epsilon_0 E + 4\pi P$$

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

$$\begin{aligned} \epsilon E &= \epsilon_0 E + 4\pi N a E \\ \epsilon &= \epsilon_0 + 4\pi N a \end{aligned}$$

now substituting from equation we get:

$$\epsilon = \epsilon_0 + (4\pi N q^2)/m \cdot [1 / \{(\omega_0^2 - \omega^2) - i\gamma\omega\}]$$

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

$$\epsilon = \epsilon' + i\epsilon''$$

From equation we get:

$$\begin{aligned} \epsilon' &= \epsilon_0 + (4\pi N q^2)/m \cdot [(\omega_0^2 - \omega^2) / \{(\omega_0^2 - \omega^2)^2 + \gamma^2 \omega^2\}] \\ \epsilon'' &= (4\pi N q^2)/m \cdot [(\gamma\omega) / \{(\omega_0^2 - \omega^2)^2 + \gamma^2 \omega^2\}] \end{aligned}$$

We have expressions for the real and imaginary parts of the complex dielectric function (ϵ' and ϵ''). What do these expressions tell us about the response of a material to electromagnetic radiation? Let us consider the frequency dependence of ϵ' and ϵ'' . The frequency dependences given by equations (1) and (2) show that, for most of the spectrum, ϵ' increases with increasing frequency. This is known as normal dispersion. However, for a small section close to the resonance frequency of the oscillator, ω_0 , the value of ϵ' decreases with increasing frequency. This is known as anomalous dispersion. The width of the region of anomalous dispersion is determined by the strength of the damping coefficient, γ . For small values of γ , the region of anomalous dispersion is narrow.

However, for large values of γ , 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 (1) and (2) also shows us that, for small values of γ , the value of ϵ'' remains small and the peak of ϵ'' is very close to the resonance frequency of the medium, ω_0 . Likewise, ϵ'' has its anomalous region centred at about ω_0 .

However, for large values of γ , the situation is quite different. With increasing γ , the height of the peak of ϵ'' becomes much larger and the peak position moves away from the resonance frequency, as does the position of the anomalous region in ϵ' . Since γ 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 γ correspond to highly absorbing media. Similarly, low values of γ 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 (1) 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 $\sim 10^{11}$ Hz (~ 3 mm) region of the spectrum; likewise the ionic polarisation affects the spectrum in the $\sim 10^{13}$ Hz ($30 \mu\text{m}$) region (the infrared); and the electronic polarisation will make contributions at $\sim 10^{15}$ ($0.3 \mu\text{m}$; UV). Therefore we expect some solids to exhibit spectral features in all these regions.

Refractive Indices of Material

There are two sets of optical constants that are closely interrelated.

These are:

1. The real and imaginary parts of the complex refractive index $n = n - ik$;
2. The real and imaginary parts of the complex dielectric function (relative permittivity) $\epsilon = \epsilon' + i\epsilon''$,

They are related by:

$$\epsilon' = n^2 - k^2 = \text{Re} [n^2]$$

$$\epsilon'' = 2nk = \text{Im} [n^2]$$

Which of these two sets of constants are most applicable depends on the material under investigation. Reflection and transmission by bulk media are best described using the complex refractive index ($n - ik$), whereas absorption and scattering by particles which are small compared with the wavelength are best

described by the complex dielectric function $\epsilon = \epsilon' + i\epsilon''$, however, they remain interchangeable. The media with which we are concerned have complex refractive indices that depend on wavelength and are complex.

We can write the refractive index, n , of a medium as:

$$n = n - ik$$

To simplify the problem we assume that we have radiation incident on our medium in the form of an idealised, sinusoidal wave.

The incident radiation can be written as:

$$A = A_0 e^{i(\omega t - 2x)}$$

where A is the amplitude, ω is the angular frequency and the wave is propagating in the positive x -direction.

Once the radiation enters the medium, the velocity of light becomes c/n , so that:

$$A = A_0 e^{i(\omega t - 2n x)}$$

$$A = A_0 e^{i\omega t - 2i(n - ik) x}$$

$$A = A_0 e^{i(\omega t - 2n x / v)} e^{-2kx}$$

From this we can see that the intensity of the wave (which is proportional to A^2) will decrease exponentially with decay constant of $4k$. Therefore the imaginary part of the refractive index, k , is directly responsible for the absorption of the light in the medium.

Scattering

Another consideration in the spectra of small particles is scattering. Consider a small particle placed in a beam of light. The intensity of the electromagnetic radiation incident on the particle is I_0 ; at a point a large distance r from the particle, the intensity of the scattered light is I . The scattered intensity I must be proportional to the incident intensity I_0 , and the inverse square of the distance $1/r^2$, hence we can say that:

$$I = [I_0 F(\theta, \phi)]/[k^2 r^2]$$

where $k = 2\pi/\lambda$ is the wavenumber, and $F(\theta, \phi)$ is an orientation dependent, dimensionless function of the direction but not distance from the particle. The total energy scattered by the particle in all directions is defined as being equal to the energy of the incident light falling on the cross-sectional area C_{sca} , where C_{sca}

is the scattering cross section. If the function $F(\theta, \phi)$ is divided by $k^2 C_{sca}$ the phase function is obtained, which has no dimensions and whose integral over all directions is 1.

Therefore:

$$C_{sca} = (1/k^2) \int F(\theta, \phi) d\omega$$

where $d\omega = \sin\theta d\theta d\phi$ is the element of solid angle and the integral is taken over all directions. In a similar way to the scattering cross-section case, the energy absorbed by the particle can be put equal to the energy incident on the area C_{abs} (the absorption cross-section). Likewise the total energy depleted from the original beam can be put equal to the incident energy on the area C_{ext} , the extinction cross-section. The law of conservation of energy requires that:

$$C_{ext} = C_{abs} + C_{sca}$$

The efficiency of a particle to absorb, scatter and extinguish are given by the Q factors, where:

$$C_{ext} = Q_{ext} \times \text{area}$$

$$C_{abs} = Q_{abs} \times \text{area}$$

$$C_{sca} = Q_{sca} \times \text{area}$$

Therefore:

$$Q_{ext} = Q_{abs} + Q_{sca}$$

The Q-factors can be calculated from the complex refractive index (or complex dielectric function) using Mie Theory

Mie Theory

Mie theory describes the way in which spherical, homogeneous particles interact with electromagnetic radiation. Certain assumptions are made about these particles in order to simplify the situation.

These assumptions are:

- Only the interactions of a single particle with light of arbitrary wavelength are considered.
- The optical properties of the particle are completely described by frequency-dependent optical constants (*i.e.* the complex refractive index or the complex dielectric function).
- Scattering is elastic, *i.e.* the frequency of the scattered light is identical to that of the incident light.

- Only single-scattering occurs. That is, each individual particle is acted on by an external field (due to the incident radiation) in isolation from the other particles. The total scattered field is merely the sum of the fields scattered by each particle (*i.e.* the particles do not affect each other).
- For a collection of particles, the number of particles is large and their separations are random, so that the waves scattered by the individual particles have no systematic phase relation.
- The medium in which the particles are embedded is considered to be:
 - a. Linear,
 - b. Homogeneous;
 - c. Isotropic.

The theory used to find the transmission spectra of small particles from the optical constants is known as Mie Theory. This calculates the Q-factors, which are the efficiency factors for extinction, scattering and absorption. There is no simple explicit formula for the Q-factors, however if $2a$, (where a is the radius of a spherical particle and is the wavelength of the incident light), then for a spherical particle:

$$Q_{\text{sca}} = (8/3)(2a)^4 \text{Re}\left\{\frac{(n^2 - 1)}{(n^2 + 2)}\right\}^2$$

$$Q_{\text{abs}} = 8a / \text{Im}\left[\frac{(n^2 - 1)}{(n^2 + 2)}\right]$$

where $n = n - ik$.

Given the close relation between the complex refractive index and the complex dielectric function, we can also write these equations in terms of the dielectric function:

$$Q_{\text{sca}} = (8/3)(2a)^4 \text{Re}\left\{\frac{(\epsilon - 1)}{(\epsilon + 2)}\right\}^2$$

$$Q_{\text{abs}} = 8a / \text{Im}\left[\frac{(\epsilon - 1)}{(\epsilon + 2)}\right]$$

where $\epsilon = \epsilon' - i\epsilon''$. There are computer programmes that use Mie Theory to evaluate the Q-factors and thus produce the relevant spectra.

These programmes require the input of:

- A dimensionless length $2a/\lambda$;
- The real and imaginary parts of the refractive index of the materials $n = n - ik$, or the real and imaginary parts of the dielectric function of the material $\epsilon = \epsilon' - i\epsilon''$.

Determination of Optical Constants

It is assumed that the optical properties of a particle are completely specified by frequency-dependent optical constants. The optical constants of minerals of astronomical significance must, therefore, be determined. This is most easily done using bulk materials, as opposed to particles, but either can be used. The data accumulated from published sources include both bulk and particulate samples and transmission, absorption and reflection spectra. It is not very useful to compare spectra measured by different techniques, especially since the appearance of the spectra depends on the measurement conditions. The transmission spectrum of a bulk medium is often very different from its particulate counterpart. The chemical composition remains the same, but the state of aggregation, and hence scattering properties, differ. The homogeneous bulk does not scatter light, however the particulate material has a transmission spectrum that may be primarily the result of scattering. Gross optical properties of a given material differ appreciably depending on its state of aggregation.

Optical theory was therefore used to normalize the data by finding the intrinsic optical constants and calculating the spectra. Since most of the astronomical spectra will be particulate, either emissive or absorptive in nature, the data can be used to calculate the spectra of such systems. There are various methods, each of which has its advantages and limitations, depending on the form of the material we are interested in, are outlined here:

- Measurement of refractive angles. The real part of the refractive index, n , can be obtained using Snell's Law. This requires the sample to be of high transparency (*i.e.* $k \sim 0$).
- Measurement of transmittance and reflectance of a slab for light at near-normal incidence. Again, the sample needs to be transparent in order to have a measurable transmission, but the transparency required is not as high as method 1.
- Measurement of reflectance at near-normal incidence over a wide range of frequencies. This involves using a Kramers-Kronig relation to obtain the phase shift of the reflected light. The sample must be highly opaque and the method requires measurements over an extended wavelength region and usually extrapolation into unmeasured regions.

- Ellipsometric techniques. These measure the amplitude ratios and phase shifts directly. They are difficult to use over large wavelength regions due to instrument limitations.
- Measurements of reflectance for incident light of various polarisation states and two oblique angles of incidence. This method generally requires large sample surfaces, although the use of this method with small surfaces has been achieved by utilising cryogenic detectors.

Many spectra have been obtained for use with astronomical observations and are therefore already the absorption/emission spectra for particulate material. However, the exact nature of the spectrum must be taken into account. While they already represent spectra of particulate material, the spectrum plot may be of percentage transmission, percentage absorption or absorption/extinction efficiency. Astronomical spectra are of the latter type, and therefore it is necessary to normalise all other spectra to this type. So, the question is, how do we generate the extinction efficiency, Q_{ext} , from the percentage absorption or transmission? Since the absorption is the inverse of the transmission, the method is essentially the same for either type of spectrum. Suppose we have a ray which passes through an infinitesimally thin region of thickness dx which causes extinction. Let the intensity of the ray entering the extinguishing region be I_v . The radiation will lose intensity through interaction between the radiation and the matter in the extinguishing region, so that the intensity of radiation emerging from the extinguishing region is $I_v + dI_v$.

The extinction coefficient, K is defined by:

$$dI_v = -K_v I_v dx$$

We can also define the optical depth, τ , as:

$$\tau_v = \int \text{pathlength } K_v dx$$

The attenuation of radiation by the effects of extinction is given by $e^{-\tau_v}$. This is essentially the absorption of the radiation.

Therefore:

$$A = e^{-\tau_v}$$

and $\ln A = -\tau_v$ where A is the absorption.

Since transmission is the inverse of absorption, $T = 1/A$, we also have:

$$\ln T = \tau_v$$

So the optical depth, τ , can be obtained from the absorption or transmission. This must then be related to the extinction efficiency, Q_{ext}

The optical depth has been defined as:

$$\tau_V = \int \text{pathlength } K_V dx$$

For a homogeneous extinguishing medium this gives:

$$\tau_V = D K_V$$

where D is the path-length, and K_V is defined as:

$$K_V = n C_V$$

where n is the number of particles per unit volume and C_V is the extinction cross-section for each particle.

$$C_V = Q_{ext} a^2$$

Hence,

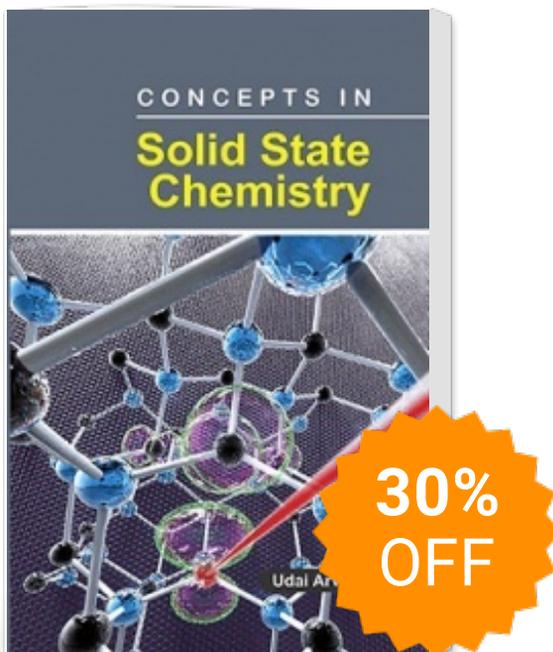
$$\tau_V = D n Q_{ext} a^2$$

and, τ_V is proportional to Q_{ext} . Therefore the shape of the extinction efficiency spectrum is identical to the shape of the optical depth spectrum and, $\ln T$ is proportional to Q_{ext} . From the transmission (or absorption) spectra we can find the shape and positions of spectral feature, however this is not a quantitative method unless the pathlength is known and the medium is homogenous.

Laboratory Spectrum

A problem has arisen regarding the laboratory spectra of some particulate materials which seems to have come about as a result of a misunderstanding of the optical properties of solids. The usual method for obtaining spectra from a particulate sample is to disperse the sample in a pellet of a substance which is transparent to light in the wavelength range of interest. This is typically potassium bromide (KBr) for mid-infrared measurements. In 1978, Dorschner undertook a study comparing the spectra of silicate samples produced using the KBr-dispersion method with spectra produced by extracting the optical constants from bulk samples. This resulted in a mismatch between the spectra, which they took to imply that the KBr embedding created a shift in the peaks of spectral features to longer wavelength. Since then the use of this correction of spectra for KBr-dispersion has been widespread, although not universal.

Concepts In Solid State Chemistry



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