CHAPTER2
NATURE OF X-RAY, X-RAY SPECTRA AND INTERACTION OF X-RAYS WITH MATTER

2.1 Brief history of development.

X-rays were discovered in 1895 by Wilhelm Conrad Rontgen at the University of Wurzburg, Bavaria. However, due to limited experimental facilities, he could not find evidences to demonstrate the obvious similarities of x-rays with light such as polarization, diffraction, reflection and refraction, So he used the designation "X" (unknown) rays. After his discovery, the nature of x-rays was gradually identified by other continuous experiments. In 1906, Barkla found evidence in scattering experiments that x-rays could be polarized and must therefore be waves, but W.H.Bragg's studies of ionization induced by x-rays indicated that they were corpuscular. In 1912, Laue and his colleagues showed that x-rays could be diffracted by a crystal that acted as a three dimensional diffraction grating. Based on diffraction experiments, W.H.Bragg found the law for the selective reflection of x-rays. These experiments demonstrated clearly the existence of a line spectrum superimposed upon a continuous ("white") spectrum of x-rays. In 1913, Moseley showed that the wavelengths of these lines were characteristic of the element of which the target was made. Soon after the first primary spectra excited by electron beams in an x-ray tube were observed, it was found that secondary fluorescent x-rays were produced in any material irradiated with beams of primary x-rays. Beginning in 1932, Hevesy, Coster and others investigated in detail the possibilities of fluorescent x-ray spectroscopy as a means of qualitative and quantitative analysis.

2.2 Nature of x-rays

X-rays may be defined as electromagnetic radiation of wavelengths ~ 10^{-5} to 100 Å produced by deceleration of high energy electrons and/or by electron transitions in the inner orbits of atoms. The 10^{-5} Å radiation is produced in betatrons operating at ~1 GV; 100 Å presents the K-band spectra of the lightest elements (Be K_α). In conventional x-ray spectrometry the spectral region of interest is about 0.1 Å (U K_α) to 20 Å (F K_α).
The properties of x-rays may be summarized as follows:

- Invisible

- Propagated in straight lines with a velocity of $3x10^8$ m/s as is light .
- Unaffected by electrical and magnetic fields.
- Differentially absorbed in passing through matter of varying composition, density, or thickness.
- Reflected, diffracted, refracted and polarized.
- Capable of ionizing gases.
- Capable of affecting electrical properties of liquids and solids.
- Capable of blackening a photographic plate.
- Able to liberate photoelectrons and recoil electrons.
- Capable of producing biological reactions, for example to damage or killing living cells and to produce genetic mutations.
- Emitted in a continuous spectrum whose short-wavelength limit is determined only by the voltage of the tube.
- Emitted also with a line spectrum characteristic of the chemical elements.
- Found to have absorption spectra characteristic of the chemical elements.

2.3 X-ray spectra

The X-rays spectra may be, based on the definition of x-rays, divided into two categories: the continuous spectrum and characteristic line spectrum.

2.3.1 The continuous spectrum

The continuous spectrum (bremsstrahlung) arises when high speed electrons undergo stepwise deceleration in matter.The X-ray tube is the principle source to produce the continuous spectrum. Deceleration of other high speed particles such as protons, alphas and ions also generates a continuum, but these sources are of little practical importance in x-ray spectrometry analysis.

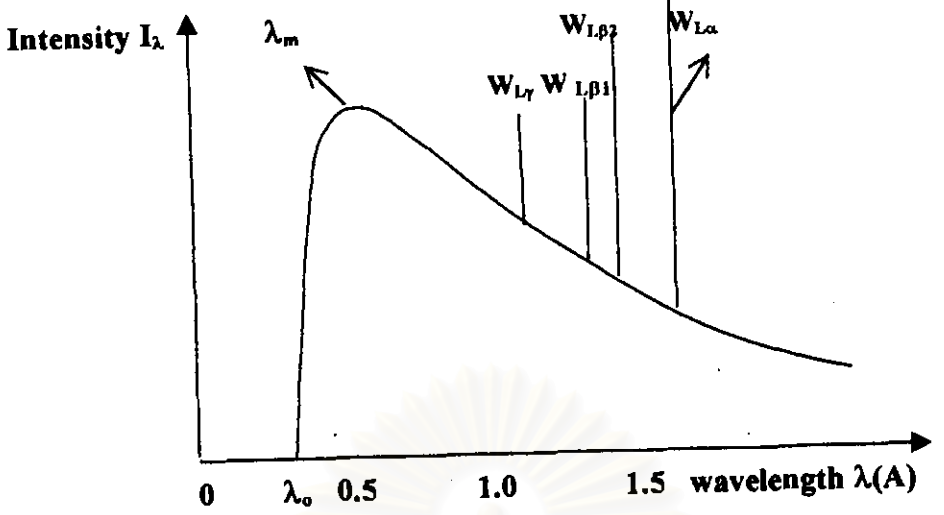

Figure 2.1 Typical emission spectrum from a W-target x-ray tube at 50 kV

In a typical x-ray continuous spectrum produced from a W-target X-ray tube operating at 50 kV, the short wavelength limit λ_o is determined by:

$$\lambda_o = hc / E_e = hc / eV \qquad (2\text{-}1),$$

where E_e=eV is kinetic energy of electrons,

V is the potential between Anode (filament) and Cathode (W-target),

h is Planck's constant and c is the velocity of light.

The equation (1.1) can be rewritten as follow:

$$\lambda_o = 12400 / V \qquad (2\text{-}2),$$

where λ_o is in Angstrom (Å) and V in Volt (V).

$W_{L\gamma 1}$, $W_{L\beta 2}$, $W_{L\beta 1}$ and $W_{L\alpha}$ are the W-characteristic lines which result from the direct ionization of the W-atoms by the impinging electrons. The properties of the continuum can be expressed by three criteria:

i) The equation (2-1), namely the Duane-Hunt law, shows that the short wavelength limit λ_o does not depend on the target material, but only depends on the potential V between Anode and Cathode.

ii) The total or integrated intensity is an increasing function of applied voltage V and atomic number Z of the target as follow:

$$I = KZV^2 \qquad (2\text{-}3),$$

where K is a constant that includes the electron current i in the tube.

iii) The spectral distribution of the continuum was derived empirically by Kulenkamff

$$I_\lambda = (KZ / \lambda^2)(\lambda / \lambda_o - 1) \qquad (2\text{-}4);$$

this equation predicts the observed maximum intensity at $\lambda_m = 1.5\lambda_o$ and it is in agreement with equation (2-3).

2.3.2 The characteristic line spectrum

The characteristic line spectrum consists of a series of discrete wavelengths-spectral lines-characteristic of the emitting element and having various relative intensity. The line spectrum of an element originates when electrons are expelled from the inner levels of its atom, and electrons from levels farther out fall into vacancies. Each such transition constitutes an energy loss which appears as an x-ray photon. For example, on creation of a K-shell vacancy, a succession of spontaneous electron transitions
follows; each fills a vacancy in a lower level with resultant emission of an x-ray photon, but also creates a vacancy in a level farther out.

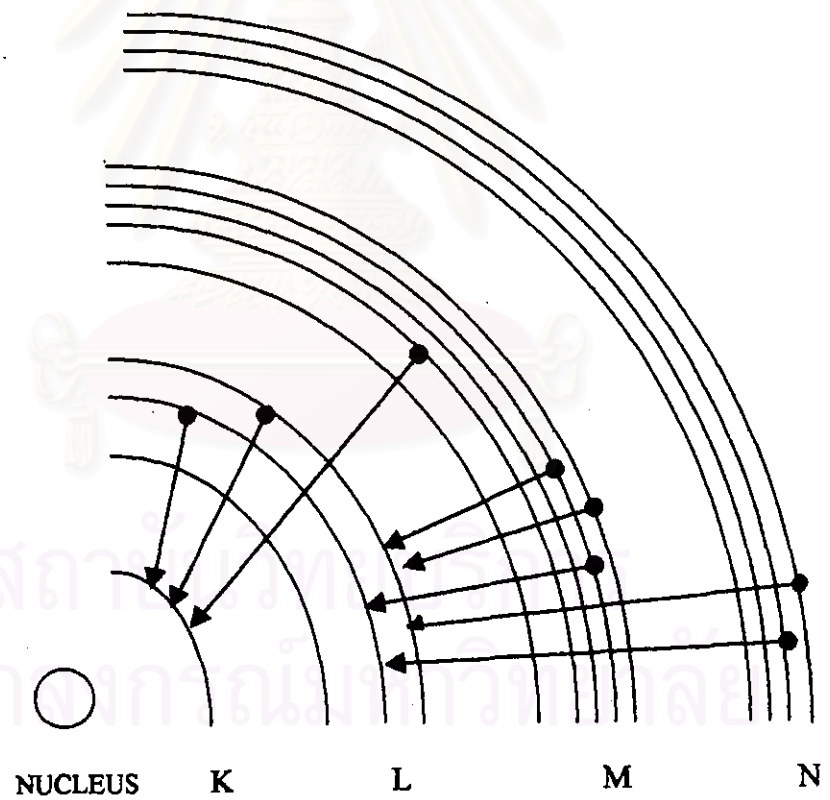

Figure 2.2 Typical series of electron transitions that may follow creation of shell vacancies

Figure 2.2 shows a series of electron transitions that may follow the creation of a K-shell vacancy. The result of this process is the simultaneous generation of the K,L,M, etc. series of x-ray spectra of the element. All lines in a series result from electron transitions from various levels to the same shell. Sometimes, series are further divided into subseries, such as L_I, L_{II}, L_{III}; All lines in a subseries result from electron transitions from various levels to the same level. However, it is also noted that electron transitions can not occur from any higher to any lower level, the permittable transitions must obey the following selection rules:

$$\Delta n \geq 1,$$

$$\Delta L = \pm 1,$$

$$\Delta J = \pm 1 \text{ or } 0.$$

Where n, L and J are the quantum numbers characteristic for the initial and final energy levels of the transition. For example, a L_{III} to L_I transition violates the first rule, or a N_{VI} (L=3) to L_I (L=0) transition violates the second rule.

2.3.3 Fluorescence yield

Due to the Auger effect, the actual number of x-ray photons produced from an atom is less than expected. The probability that a vacancy in an atomic shell or subshell is filled through a radiative transition is called the fluorescence yield. The fluorescence yield of the K-shell, therefore, is:

$$\omega_K = I_K/n_K \qquad (1\text{-}5);$$

where I_K is the total number of characteristic K x-ray photons emitted from a sample and n_K is the number of primary K-shell vacancies.

The definition of the fluorescence yield of higher atomic shells is more complicated for the following two reasons:

i. Shell above K-shell consist of more than one subshell; the average fluorescence yield depends on how the shells are ionized.

ii. Coster-Kronig transitions which are non-radiative transitions between the subshells of an atomic shell having the same principal quantum number.

Although in principle the K-shell fluorescence yield ω_K can be calculated theoretically, experimental data are often applied in practice. The following semi-

empirical equations given by Burhop may be used to calculate the K-shell fluorescence yield:

$$[\omega_K / (1-\omega_K)]^{1/4} = 0.064 + 0.034\ Z - 1.03\times10^{-6}\ Z^3 \qquad (2\text{-}6);$$

or from a different equation:

$$[\omega_K / (1-\omega_K)]^{1/4} = -0.217 + 0.03318\ Z - 1.14\times10^{-6}\ Z^3 \qquad (2\text{-}7),$$

which gives quite good agreement with the experimental values for almost all elements. Other useful expressions for calculation of the fluorescence yields ω_K ($12 \leq Z \leq 42$) and ω_{LIII} ($38 \leq Z \leq 79$) have recently been found, based on literature and experimental data:

$$\omega_K = 0.33704 - 0.060047\ Z + 0.0033133\ Z^2 - 3.9251\times10^{-5}\ Z^3 \qquad (2\text{-}8),$$

$$\omega_{LIII} = 0.0441 - 0.0047559\ Z + 1.1494\times10^{-4}\ Z^2 - 1.8594\times10^{-7}\ Z^3 \qquad (2\text{-}9),$$

2.3.4 Absorption jump ratio

$$r_k = (\mu/\rho)_K + (\mu/\rho)_{LI} + (\mu/\rho)_{LII} + (\mu/\rho)_{LIII} + \ldots / (\mu/\rho)_{LI} + (\mu/\rho)_{LII} + (\mu/\rho)_{LIII} + \ldots$$

$$\equiv (\mu/\rho)_S / (\mu/\rho)_L \qquad (2\text{-}10),$$

$r = (\mu/\rho)_S / (\mu/\rho)_L$ is called absorption edge jump ratio,

$\delta = (\mu/\rho)_S - (\mu/\rho)_L$ is jump difference. (2-11),

Therefore, actual fraction of the total number of photo-ionization that occurs in the K shell is given by:

$$(\mu/\rho)_S - (\mu/\rho)_L / (\mu/\rho)_S = 1 - (\mu/\rho)_L / (\mu/\rho)_S$$

$$= 1 - 1/r_k$$

$$= (r_k - 1) / r_k \qquad (2\text{-}12),$$

2.4 Phenomena in interaction of x-rays with matter

2.4.1 Attenuation of x-rays

If a parallel monochromatic x-ray beam of intensity I_o (Fig. 2.3) is directed on a given homogeneous material, after passing through a thickness X of the material, its intensity is reduced to I_x due to the absorption and scattering phenomena. This attenuation process obeys the Lambert law as follow:

$$dI / I = -\mu_l dx \qquad (2\text{-}13),$$

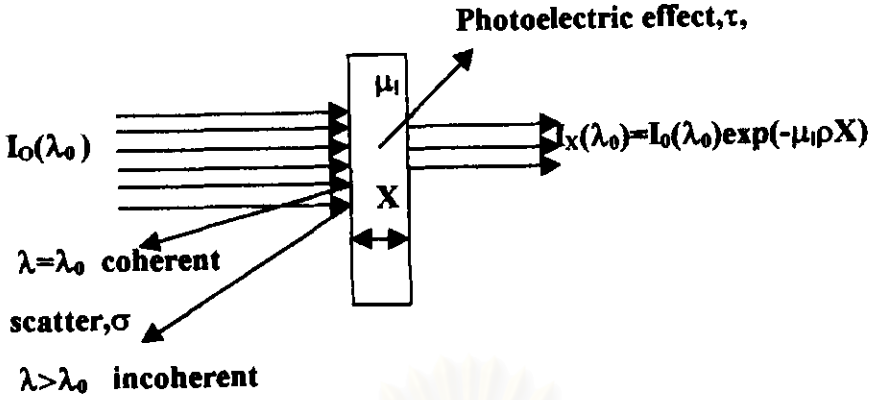

Figure 2.3 Transmission of x-rays through a layer of material

After integration over the path length X we have:

$$I_x = I_o \exp(-\mu_l X) \qquad (2\text{-}14),$$

where μ_l is the linear attenuation coefficient of the material at that wavelength (cm^{-1}).

If $\rho(g/cm^3)$ is the material density, then equation (1-6) can be written as :

$$I_x = I_o \exp[(-\mu_l/\rho)\rho X] \qquad (2\text{-}15),$$

put $\mu = \mu_l/\rho$ that is called the mass attenuation coefficient (cm^2/g), then

$$I_x = I_o \exp(-\mu\rho X) \qquad (2\text{-}16),$$

the fraction $I_o - I_x$ of the intensity that is not transmitted in the same direction as the incident photons is lost mainly by two following processes: (1) Absorption of a number of incident x-ray photons that are annihilated in expelling an equal number of orbital electrons from the atoms. This is the photoelectric effect. The electronic rearrangement in the ionized atoms gives arise to x-ray fluorescence emission and Auger absorption. (2) Scattering of the incident photons in all directions after collision with atoms. The scattered photons have either a longer wavelength (incoherent) or the same wavelength (coherent or Rayleigh scattering).

Thus, the mass attenuation coefficient μ can be regarded as the sum of two coefficients:

$$\mu = \tau + \sigma \qquad (2\text{-}17);$$

where τ is the mass photoelectric absorption coefficient,

σ is the mass scattering coefficient.

2.4.2 Photoelectric absorption - absorption edges

In the photon energy range between 0 and 100 keV considered here, the photoelectric absorption coefficient is several times greater than the scattering coefficient and often accounts for at least 95% of the attenuation coefficient μ. For that reason, the experimental values of the attenuation coefficient adequately reflect the properties of the photoelectric coefficient. For example of tungsten in figure 1.4, τ increases rapidly with wavelength. This indicates that the probability of a photon ejecting an electron from atom increases when its energy decreases. However, within certain limit of energy the sharp discontinuities of the probability are observed in the absorption curve. They are related to the critical excitation energies and their corresponding wavelengths.

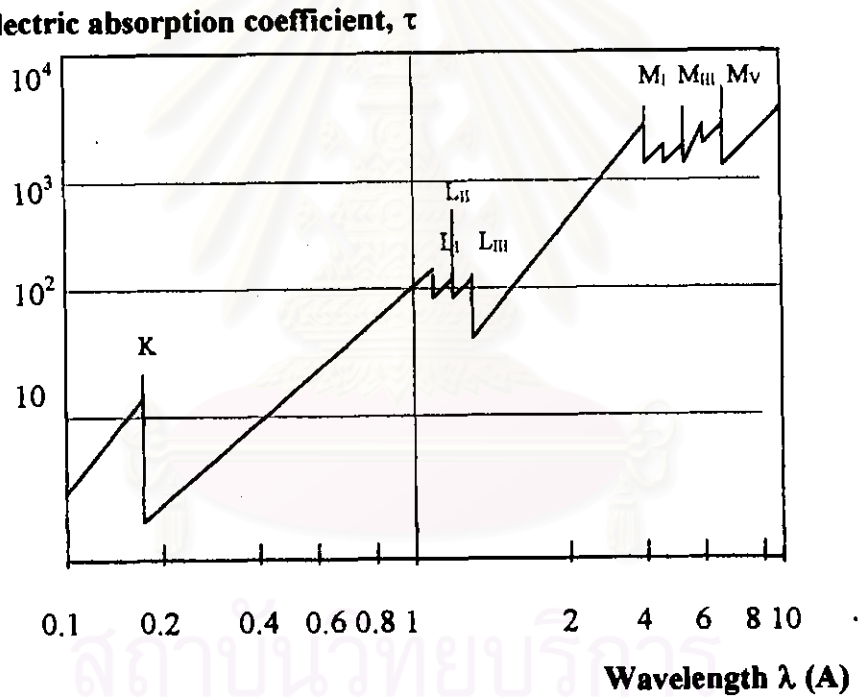

Figure 2.4 Photoelectric absorption coefficient of W as a function of wavelength

We can see in figure 2.4 from left to right, i.e. in the direction of decreasing of wavelength. At λ=6.89Å (E=1.8 keV) the critical value for excitation of the M_V energy level is reached and ionization at this level is possible. The sharp increase of the absorption coefficient at this energy is called the M_V absorption edge. For the same reason, the M_{IV} to M_I absorption edges are observed at wavelengths between 6.89 and

4.43 Å (or at energies between 1.8 and 2.8 KeV). Wavelengths of 1.22, 1.08 and 1.02 A are necessary to excite the L_{III}, L_{II} and L_I levels, respectively and consequently three corresponding absorption edges are observed. The K-absorption edge is reached at λ= 0.18 Å (E=69.5KeV). From then on, the absorption decreases to very low values as the energy approaches infinity.

2.4.3 Scattering

Scattering includes two phenomena: (1) coherent scattering (also known as unmodified, elastic or Rayleigh scatter) in which the x-ray photons are deflected without loss of energy, that is, without increase of wavelength. (2) incoherent scattering (also known as modified, inelastic or Compton scatter) in which x-ray photons are deflected with loss of energy and increase in wavelength. The linear scattering coefficient is given by:

$$\sigma = Zf^2 + (1 - f^2) \qquad (2\text{-}18),$$

where two right terms present, respectively, the contributions of coherent and incoherent scattering; f is electronic structure factor, that is, the scatter power of an electron.

2.4.3.1 Coherent and incoherent scattering

Coherent scattering occurs when the incident x-rays cause bound atomic electrons in the irradiated matter to oscillate at the same frequency as the x-rays. In this process the atom is neither ionized nor excited. The oscillating electrons emit x-rays in all directions again at the same frequency. The intensity of the radiation scattered by an atom is determined by summing the amplitudes of the radiation coherently scattered by each of the electrons bound in the atom. Coherent scattering occurs mostly at the low energies and for high-Z materials.

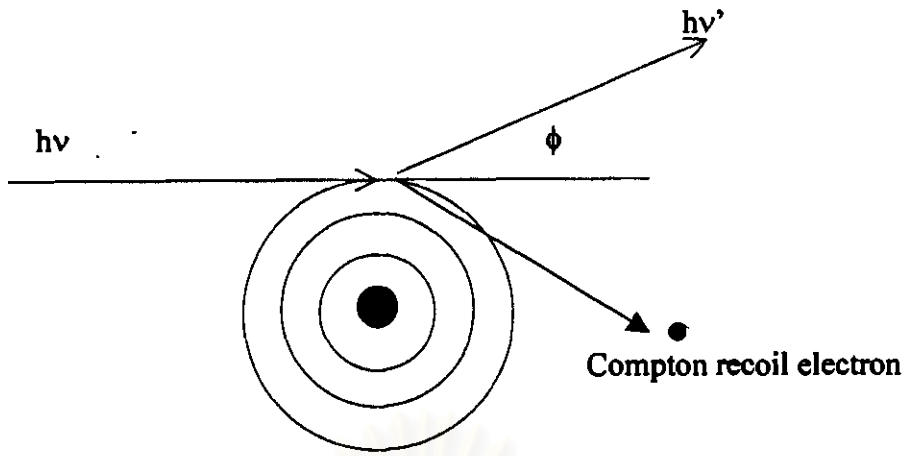

Figure 2.5 Compton scattering of an incident x-ray photon

The mechanism of incoherent scattering (or Compton scattering) is shown in figure 2.5, in which the incident x-ray photon collides with a loosely bound electron in an outer orbit of atom. The electron recoiled under the impact leaves the atom and carries away some of the energy of the photon. The incident photon is deflected with corresponding loss of energy or increase in wavelength that can be found by the laws of conservation of energy and momentum as:

$$\lambda' - \lambda = \Delta\lambda = (h / mc)(1 - \cos\phi) \qquad (2\text{-}19);$$

where λ and λ' are wavelengths (cm) of the incident and incoherently scattered x-rays, respectively, ϕ is the angle (degree) between unscattered and scattered x-rays, m is the electron mass. The experiments indicated that (1) the proportion of Compton scattering increases as the energy of the radiation increases or as the atomic number of the scatterer decreases and coherent scattering increases as the radiation energy decreases or as the atomic number of the radiator increases; (2) the $\Delta\lambda$ is independent of both x-ray wavelength and atomic number of the scatterer , and varies only with ϕ. Incoherent scattering predominates when the x-ray energy greatly exceeds the binding energy of the orbital electrons. In turn, when this binding energy approaches or exceeds the x-ray energy, coherent scattering predominates.

2.4.3.2 Diffraction by crystals

In the x-ray spectrometer , the analyzer crystal disperses the secondary characteristic x-ray beam so that each wavelength may be measured individually. Diffraction arises from interference of coherently scattered x-rays. According to Bragg's point of view for diffraction phenomenon, it may be regarded in terms of reflection of a x-ray beam from a stack of crystal planes. As a collimated monochromatic x-ray beam of wavelength λ is directed at angle θ on a set of crystal planes(hkl)(figure 2.6), it is scattered in all directions from each plane, but only in certain directions occurs so-called scatter reinforce, i.e. the rays are in phase and the resultant ray has the same wavelength as the individual x-rays and the peak amplitude equal to sum of the amplitudes of the constituent x-rays. The group of thus reinforced rays constitutes a diffracted x-ray beam. The mentioned-above diffraction phenomenon may be occurred only under the conditions given by Bragg as follow: (1) the angles made by the diffracting planes (hkl) with the incident and diffracted beams are equal; (2) the directions of the incident and diffracted beams and the normal to the diffracting planes are coplanar; (3) reflected rays from successive planes differ in path length by an integral number of wavelengths:

$$n\lambda = 2d\sin\theta \ (\equiv CBD) \qquad (2\text{-}20),$$

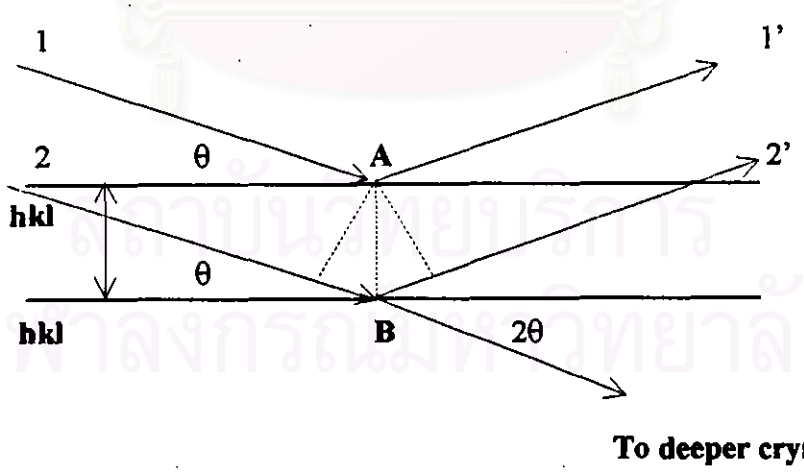

Figure 2.6 Diffraction by crystal according to Bragg's description.

diffraction phenomenon becomes an important physical basic to produce the wavelength dispersive x-ray fluorescence (WDX) spectrometers. In practice, the x-ray spectrometers are usually calibrated in terms of 2θ, the angle between the diffracted beam and the undeflected incident beam.