Chapter 5. Crystal Structure

5-1. Structure of Metal and Element

- Crystal structures may be described in a number of ways. The most common manner is to refer to the size and shape of the unit cell and the positions of the atoms (or ions) within the cell.
- However, this information is sometimes insufficient to allow for an understanding of the true structure in three dimensions.
- Consideration of several unit cells, the arrangement of the atoms with respect to each other, the number of other atoms they in contact with, and the distances to neighboring atoms, often will provide a better understanding.
- A number of methods are available to describe extended solid-state structures. The most applicable with regard to elemental and compound semiconductor, metals and the majority of insulators is the close packing approach.

5-1-1. Cubic close packed: face-centered cubic

- For another method, if the stacking order is ABCABCABC....., then this close-packing is called **'cubic close-packing'**.
- Figure 2-5 shows the unit cell with lattice constant 'a', and the coordinates of atoms are (0, 0, 0), (1/2, 1/2, 0), (1/2, 0, 1/2) and (0, 1/2, 1/2).
- The number of atoms per unit cell is '4' and the nearest coordination number is '12'.
- If the close-packing stacking direction is the diagonal of a cube, then the structure will be **face-centered cubic(fcc)** structure as shown in Fig. 2-5(b).

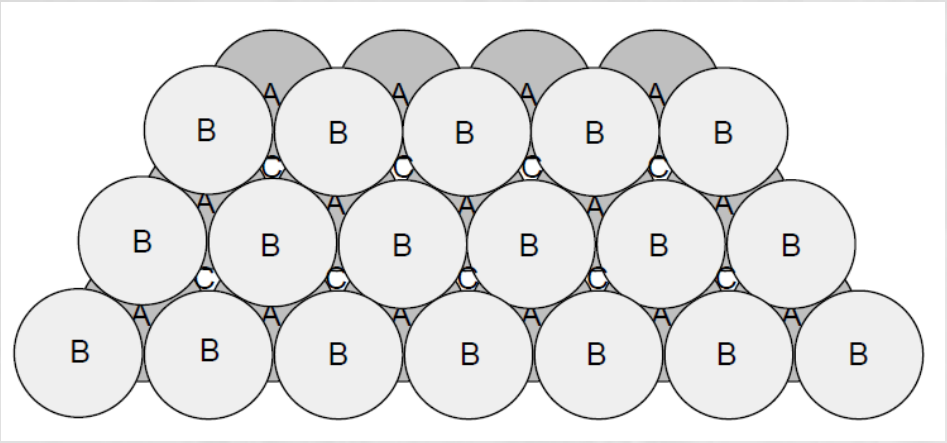


그림 2-3(b) 3 차원에서 구를 조밀 충전하는 방법, Cubic close-packing(CCP).

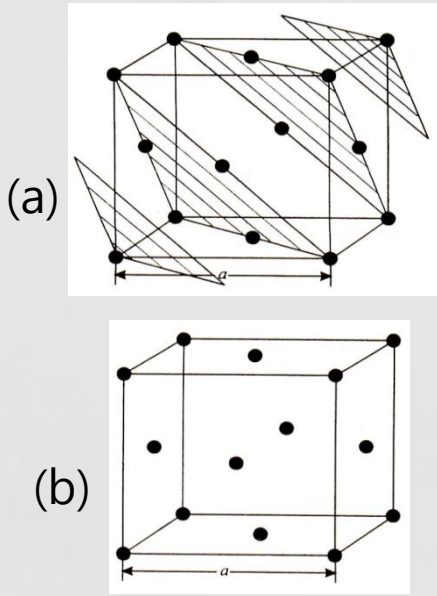


그림 2-5(b) 면심입방구조.
(a)의 빗금진 면이 조밀 충전 면임.

- The unit cell of cubic close packed structure is actually that of a face-centered cubic (*fcc*) Bravais lattice.
- In the *fcc* lattice the close packed layers constitute the {111} planes.
- As with the *hcp* lattice packing fraction in a cubic close packed (*fcc*) cell is 74.05%. Since face centered cubic or *fcc* is more commonly used in preference to cubic close packed (*ccp*) in describing the structures, the former will be used throughout this text..
- In both *fcc* and *hcp* lattices each of the atoms have a coordination number of 12.
- The distance between the nearest atoms is $a/\quad \sqrt{2}R$.

Octahedral and tetrahedral vacancies

- As was mentioned above, the packing fraction in both *fcc* and *hcp* cells is 74.05%, leaving 25.95% of the volume unfilled.
- The unfilled lattice sites (interstices) between the atoms in a cell are called interstitial sites or vacancies.
- The shape and relative size of these sites is important in controlling the position of additional atoms.
- In both *fcc* and *hcp* cells most of the space within these atoms lies within two different sites known as octahedral sites and tetrahedral sites.
- The difference between the two lies in their “coordination number”, or the number of atoms surrounding each site.
- Tetrahedral sites (vacancies) are surrounded by four atoms arranged at the corners of a tetrahedron. Similarly, octahedral sites are surrounded by six atoms which make-up the apices of an octahedron.
- For a given close packed lattice an octahedral vacancy will be larger than a tetrahedral vacancy.

- Within a face centered cubic lattice, the eight tetrahedral sites are positioned within the cell, at the general fractional coordinate of $(^n/_4, ^n/_4, ^n/_4)$ where n = 1 or 3, e.g., $(^1/_4, ^1/_4, ^1/_4)$, $(^1/_4, ^1/_4, ^3/_4)$, etc as shown in Fig. 5-1(a).
- At these vacant sites, the largest radius of sphere could be $r = (\sqrt{3/2} - 1)R = 0.225R$ ere are 4 spheres surrounding the vacancy.
- That's why this vacant sites are called 'tetrahedral sites'
- Metals Cu, Ag, Au, Al, Pb, transition matals Co, Ni, Rh, Pt, Pd, Ir, and inert elements Ne, Ar, Kr, Xe have face centered cubic structure.

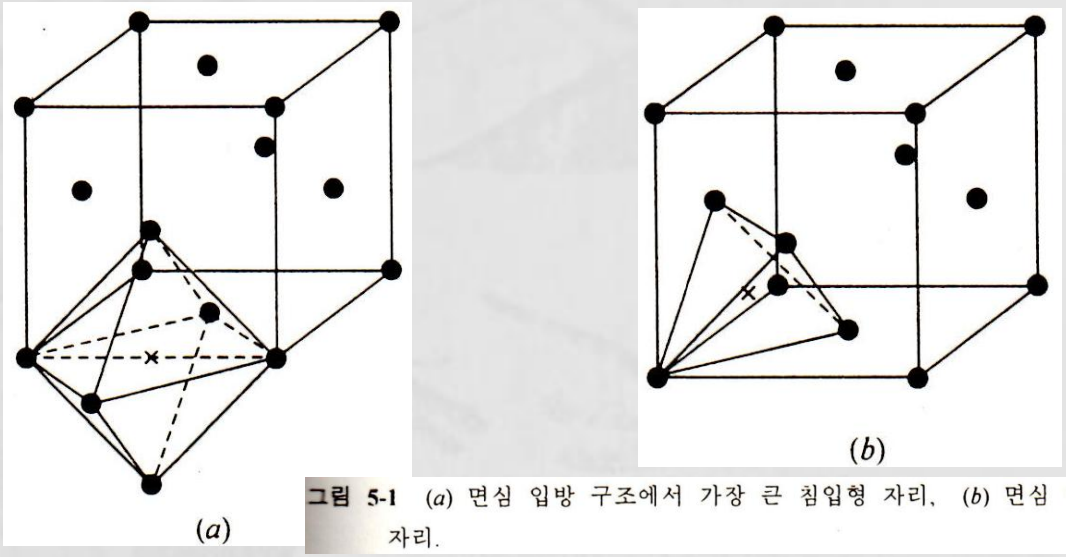
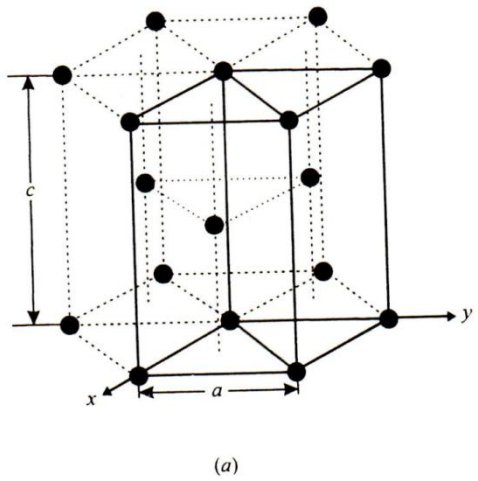


그림 5-1 (a) 면심 입방 구조에서 가장 큰 침입형 자리, (b) 면심 입방 구조에서 두번째로 큰 침입형 자리.

5-1-2. Hexagonal close packed structure

- If two close packed layers A and B are placed in contact with each other so as to maximize the density, then the spheres of layer B will rest in the hollow (vacancy) between three of the spheres in layer A as shown in Fig. 2-4.
- The octahedral sites are located at the center of the unit cell ($^1/_2$,$^1/_2$,$^1/_2$), as well as at each of the edges of the cell, e.g., ($^1/_2$,0,0).
- In the hexagonal close packed system, the tetrahedral sites are at (0,0,$^3/_8$) and ($^1/_3$,$^2/_3$,$^7/_8$), and the octahedral sites are at ($^1/_3$,$^1/_3$,$^1/_4$) and all symmetry equivalent positions.



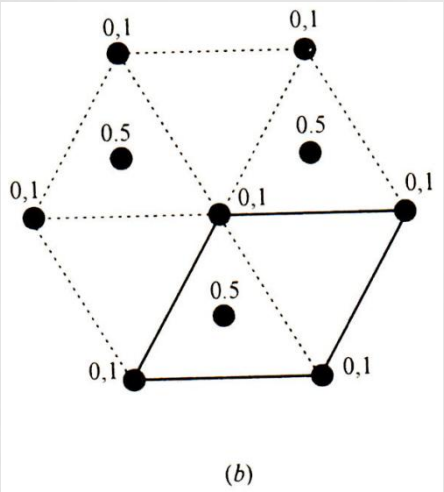


그림 2-4 (*a*) 육방 조밀 충전, (*b*) 육방 조밀 충전을 *c* 축 방향에서 본 그림.

5-1-2. Hexagonal close packed structure

나사축 6_3은 단위포에서 위치 $\frac{1}{3}\ \frac{2}{3}\ z$에 있다. 6_3는 c 축 방향으로 60° 회전 대칭과 $F/2$ 병진 대칭 작동이 결합한 대칭을 나타낸다. 그림 5-2에서 (*a*)는 6_3 나사축을 보여주고, (*b*)는 세 원자층을 c 축에 수직한 (0001) 면에 투사한 그림으로 여기서 숫자는 원자의 높이를 나타낸다.

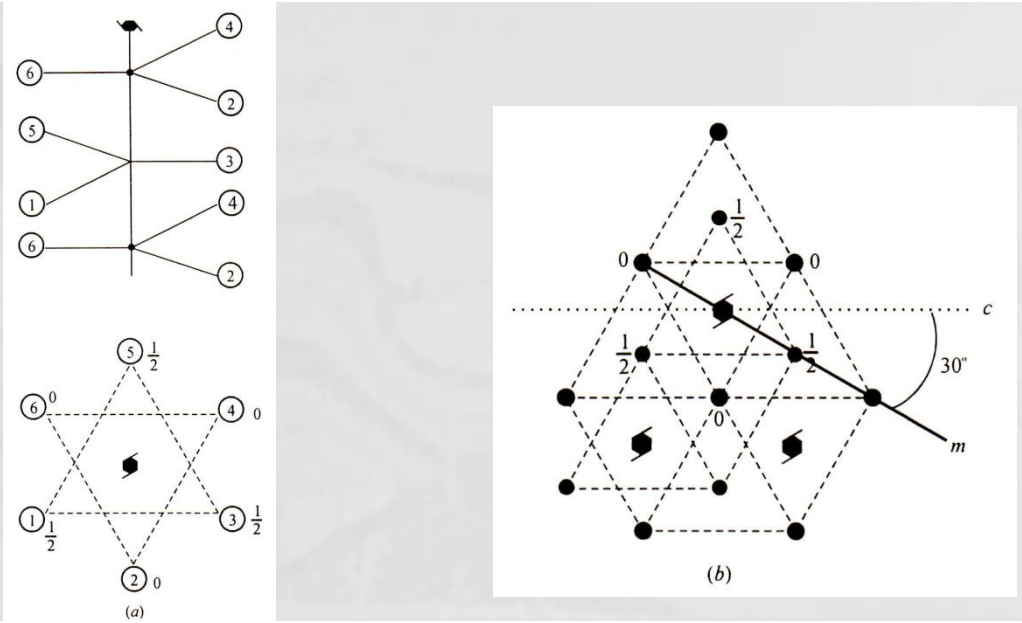


그림 5-2 (*a*) 6_3 나사축을 나타낸 그림으로 아래 그림은 위 그림의 투사이다. (*b*) 육방 조밀 충전의 4 원자층을 (0001) 면에 투사한 그림.

- The octahedral sites are located at the center of the unit cell ($^1/_2$,$^1/_2$,$^1/_2$), as well as at each of the edges of the cell, e.g., ($^1/_2$,0,0).
- In the hexagonal close packed system, the tetrahedral sites are at (0,0,$^3/_8$) and ($^1/_3$,$^2/_3$,$^7/_8$), and the octahedral sites are at ($^1/_3$,$^1/_3$,$^1/_4$) and all symmetry equivalent positions.

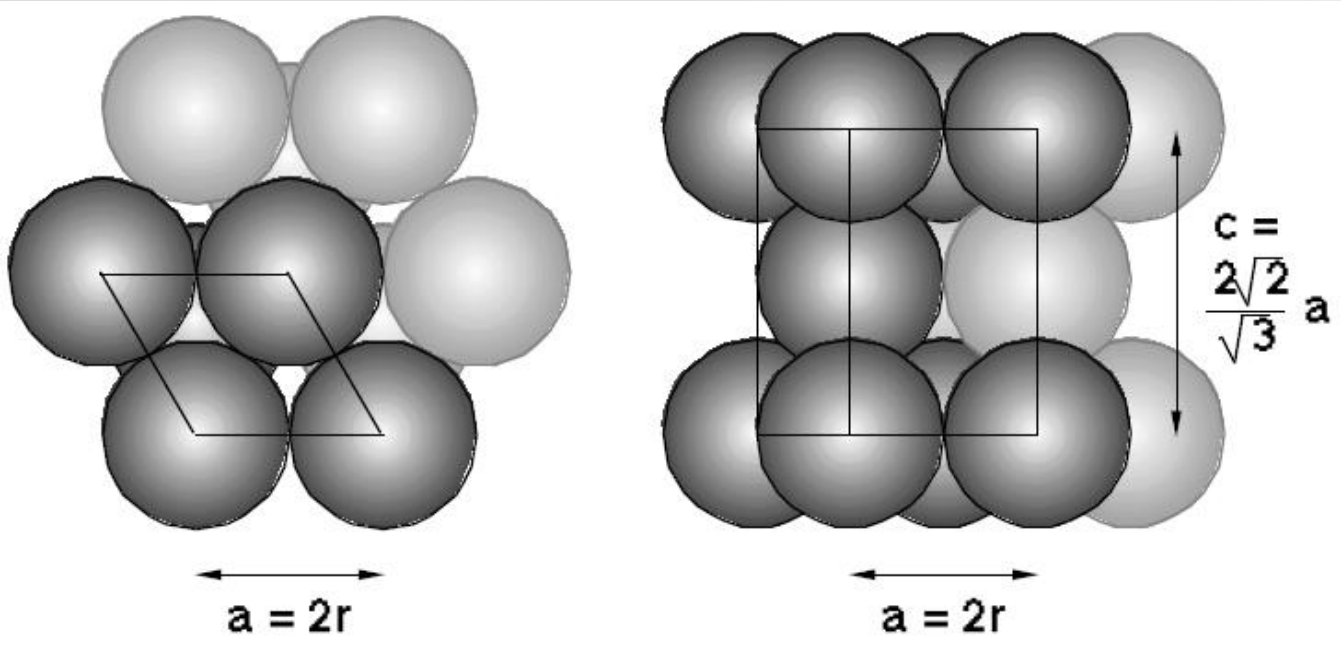


그림 2-4-1 (a) Second "A" layer (0001). (b) Front view of HCP structure

- The axis ratio c/a is equal to $\sqrt{8/3} = 1.633$
- The "packing fraction" in a hexagonal close packed cell is 74.05%.
- In both *fcc* and *hcp* lattices each of the atoms have a coordination number of 12.

- In both *fcc* and *hcp* cells most of the space within these atoms lies within two different sites known as octahedral sites and tetrahedral sites.
- Tetrahedral sites (vacancies) are surrounded by four atoms arranged at the corners of a tetrahedron. Similarly, octahedral sites are surrounded by six atoms which make-up the apices of an octahedron.
- For a given close packed lattice an octahedral vacancy will be larger than a tetrahedral vacancy.
- The coordinates of the largest vacant sites are (1/3, 2/3,1/4) and (1/3, 2/3, 3/4), and the largest radius of sphere could be

$$r = (\sqrt{2} - 1)R = 0.414R$$

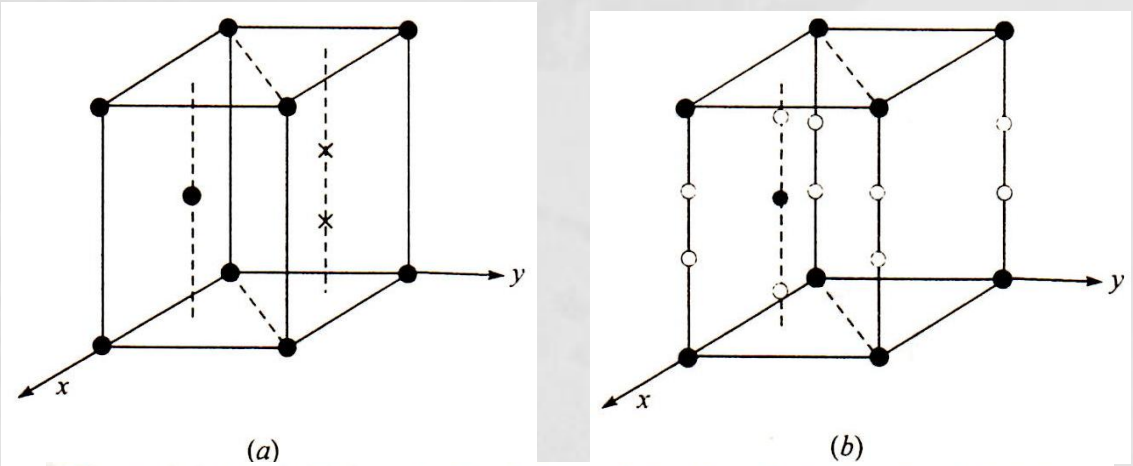


그림 5-3 육방 조밀 충전에서 침입형 자리. 가장 큰 침입형 자리는 ×로 표시하고 두번째 큰 침입형 자리는 흰 원으로 표시하였다.

5-1-3. Body centered cubic structure

- The **body-centered cubic** system (I) has one lattice point in the center of the unit cell in addition to the eight corner points. It has a net total of 2 lattice points per unit cell ($\frac{1}{8} \times 8 + 1$).
- In a *bcc* lattice, the atomic packing factor is 0.680, and in *fcc* it is 0.740.
- The coordination number of each atom in the structure is 8: the central cation is coordinated to 8 anions on the corners of a cube as shown n Fig. 5-4.

Chapter. 7 Wave and Diffraction

7-1 Wave and Fourier Transformation
7-2 Diffraction of Waves

7-1 Wave and Fourier Transformation

앞에서 배운 결정의 원자 배열과 결정 결함은 그 크기가 수 1/10 nm 단위이므로, x-선이나 전자 빔을 이용한 회절 실험으로 얻어지는 회절상에서 결정의 원자 배열과 결함을 알아낼 수 있다. 회절은 파와 결정의 상호 작용으로 일어나므로 먼저 파에 대해서 알아보자.

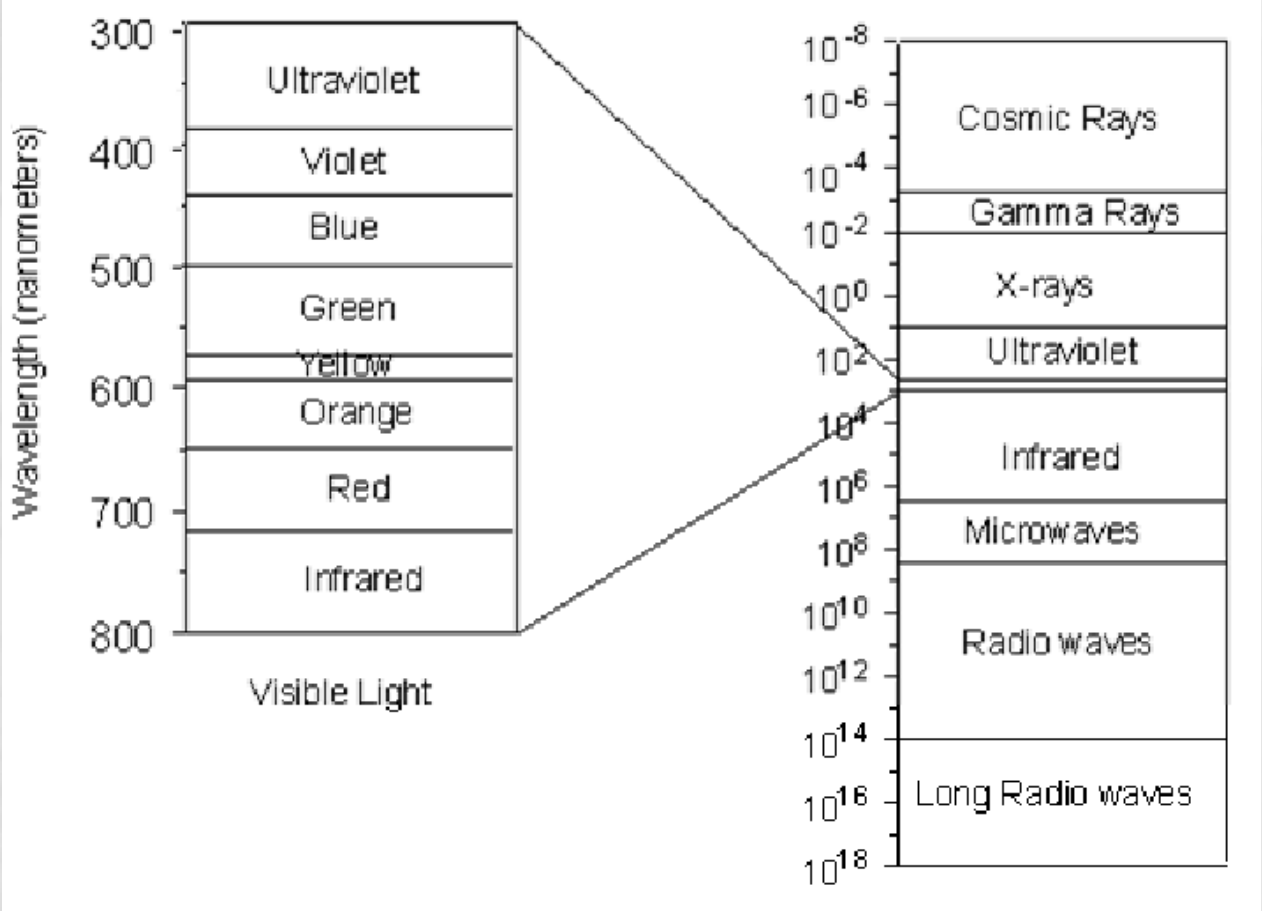
양끝이 고정되어 있는 바이올린 선의 진동을 나타내는 파는 간단히 정현(sin)파로

$$y = A \sin \frac{2\pi}{\lambda} x = \psi(x) \qquad (7\text{-}1)$$

로 나타낼 수 있으며, 이 파는 x 만의 함수이다. 그러나 일반적인 파는 시간 또는 공간 속에서 진행되는 어떤 변화이다. 이 변화를 함수 $\psi(x, t)$로 나타낼 수 있는데, 여기서 x는 어떤 공간 좌표, t는 시간 좌표이다.

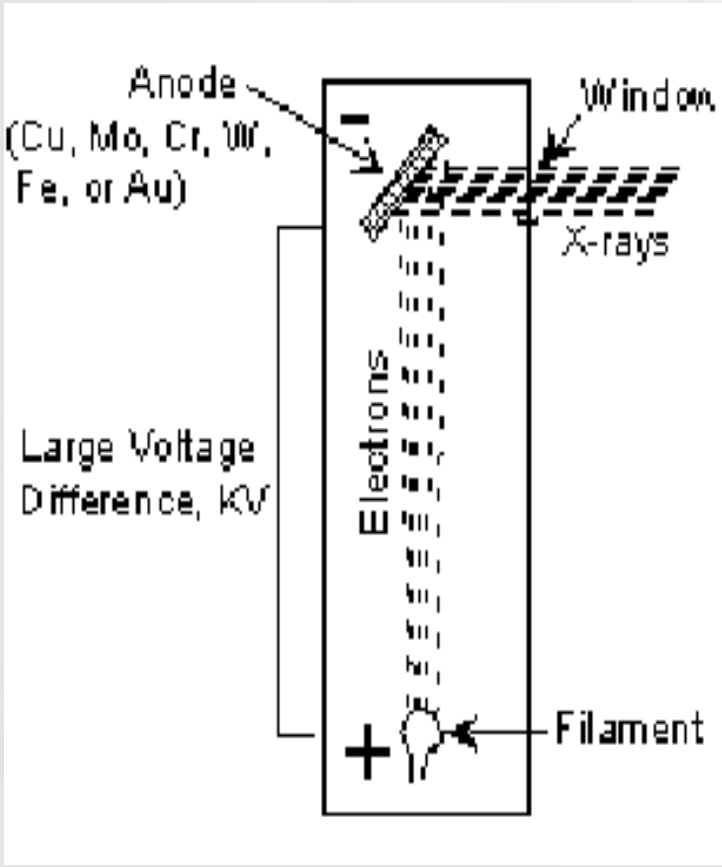
X-rays and the Production of X-rays

- 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 colors). Because X-rays have wavelengths similar to the size of atoms, they are useful to explore within crystals.


Wavelength (nanometers)
300
400
500
600
700
800
Ultraviolet
Violet
Blue
Green
Yellow
Orange
Red
Infrared
Visible Light
10^{-8}
10^{-6}
10^{-4}
10^{-2}
10^{0}
10^{2}
10^{4}
10^{6}
10^{8}
10^{10}
10^{12}
10^{14}
10^{16}
10^{18}
Cosmic Rays
Gamma Rays
X-rays
Ultraviolet
Infrared
Microwaves
Radio waves
Long Radio waves

- The energy of X-rays, like all electromagnetic radiation, is inversely proportional to their wavelength as given by the Einstein equation: $E = h\nu = hc/\lambda$
- where E = energy
  h = Planck's constant, 6.62517×10^{-27} erg·sec
  ν = frequency
  c = velocity of light = 2.99793×10^{10} cm/sec
  λ = 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, thus fractures can be seen in X-ray pictures).

- 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.

7-1-2 Fourier Transformation

주어진 함수 $f(x)$가 적분

$$f(x) = \int_{-\infty}^{\infty} a(k) \exp(2\pi i k x)\, dk \tag{7-29}$$

로 표시할 수 있도록 어떤 함수 $a(k)$가 존재한다면 $a(k)$를 $f(x)$의 푸리에 변환이라 하고 $\tilde{f}(k)$로 나타낸다. 수학적으로 표시하면 다음과 같다.

$$\tilde{f}(k) = \int_{-\infty}^{\infty} f(x) \exp(-2\pi i k x)\, dx = \mathcal{F}[f(x)]. \tag{7-30}$$

더 상세한 푸리에 변환에 대해서는 다른 참고서를 참고하기 바란다.

참고로 저자에 따라서 푸리에 변환의 정의를 약간 달리 하는 경우가 있다. $k = 2\pi/\lambda$ 를 k'으로 정의하면 지수 속에 2π를 계속 쓸 필요가 없다. 이 경우,

$$f(x) = \int_{-\infty}^{\infty} a(k') \exp(ik'x)\, dk' \tag{7-31}$$

$$\tilde{f}(k') = a(k') = \frac{1}{2\pi}\int_{-\infty}^{\infty} f(x)\,\exp(-ik'x)\,dx = \mathcal{F}[f(x)] \tag{7-32}$$

가 된다.

그러면 몇 개의 간단한 함수의 푸리에 변환을 해 보고 그것의 의미를 살펴보자. 그림 7-3(*a*)와 같이 높이가 A이고 폭이 a인 중절모 함수인 방형의 함수를 생각하자. 우함수로 이 함수를 나타내기 위해 다음과 같이 구간을 잡아보자.

$$f(x) = \begin{cases} A, & -\dfrac{a}{2} \le x \le \dfrac{a}{2} \\ 0, & x > \dfrac{a}{2},\ x < -\dfrac{a}{2}. \end{cases} \tag{7-33}$$

그러면 이것의 푸리에 변환은

$$\tilde{f}(k) = \int_{-\infty}^{\infty} f(x)\ \exp\ (-2\pi ikx)\ dx$$

$$= \int_{-\infty}^{-\frac{a}{2}} 0\ dx + \int_{-\frac{a}{2}}^{\frac{a}{2}} A\ \exp\ (-2\pi ikx)\ dx + \int_{\frac{a}{2}}^{\infty} 0\ dx$$

$$= \frac{A}{-2\pi ik}\ \exp\ (-2\pi ikx)\Big|_{-\frac{a}{2}}^{\frac{a}{2}}$$

$$= \frac{A}{-2\pi ik}\{\exp\ (-\pi ika) - \exp\ (\pi ika)\}$$

$$= \frac{A}{-2\pi ik}\{\cos\ \pi ka - i \sin\ \pi ka - \cos\ \pi ka - i\ \sin\ \pi ka\} \qquad (7\text{-}34)$$

$$= \frac{A}{-2\pi ik}(-2i\ \sin\ \pi ka) = \frac{A}{\pi k} \sin\ \pi ka$$

$$= Aa \frac{\sin\ \pi ka}{\pi ka}$$

$$\delta(x) = \begin{cases} \infty, & x = 0 \\ 0, & x \neq 0 \end{cases} \tag{7-37}$$

이고 음의 무한대에서 양의 무한대까지의 적분값이 1 인 함수로 정의한다. 즉

$$\int_{-\infty}^{\infty} \delta(x)\,dx = 1\,. \tag{7-38}$$

폭이 a 이고 높이가 a^{-1} 인, 즉 면적이 $aa^{-1} = 1$ 인 중절모 함수에서 폭 a 를 점점 줄여보자. 이 푸리에 변환은

$$\tilde{f}(k) = \lim_{a \to 0} a^{-1} a \frac{\sin(\pi k a)}{(\pi k a)} = 1 \tag{7-39}$$

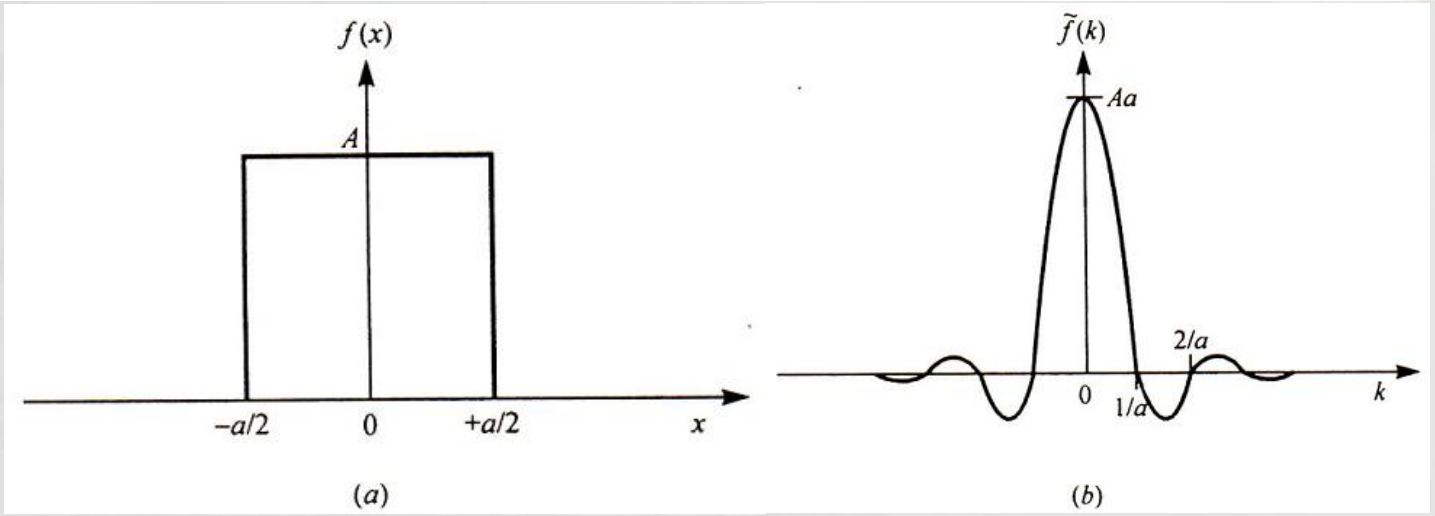


그림 7-3 (*a*) 높이가 A 이고 폭이 a 인 중절모 함수인 방형의 함수 $f(x)$, (*b*) (*a*)에 나타낸 중절모 함수의 푸리에 변환. 최대 높이는 사각형의 넓이인 Aa 와 같고 $k = n/a$, 즉 $k = \pm 1/a, \pm 2/a, \pm 3/a, \cdots$ 일 때 변환값은 0 이 된다. $f(x)$를 우함수로 만들어 주었기 때문에 변환 $\tilde{f}(k)$은 실수가 된다.