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Faculty of Materials Science and Engineering

Materials Characterization Methods

Third Session
(X-Ray and Its Application in Crystallography)

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Introduction

X-rays were discovered in 1895 by the German physicist Röntgen and were called X-rays because the nature of the rays was unknown at that time. This radiation is sometimes called Röntgen radiation.

X-rays travel in a straight line similar to normal light and also affect the photographic film, but unlike light, it is invisible.

The penetration of X-ray into materials is very high, unlike normal light, and it easily passes through the human body, boards, metals and other opaque materials.

Introduction

X-ray is used to study the internal structure opaque materials. The photographic film is placed on one side of the object and X-rays are projected on it from the other side. The resulting image on the film is due to less radiation passing through dense parts compared to more radiation passing through less dense parts of the object. The amount of radiation passing through different materials also varies. This method is called radiography.

Introduction

Using radiography, the location of fractures in bones and cracks and impurities in different materials and parts can be studied.

In 1912, the nature of X-rays was determined and the diffraction of these rays was detected by crystal materials.

X-ray radiography to study the internal structure of the material is limited to the minimum dimensions of 0.1 cm, but the diffraction method provides the possibility of studying up to dimensions of 10^{-8} cm.

X-Ray Production

X-ray is a type of electromagnetic radiation with a spectrum similar to normal light but with a much shorter wavelength than light (0.5-2.5 angstroms compared to 6000 angstroms).

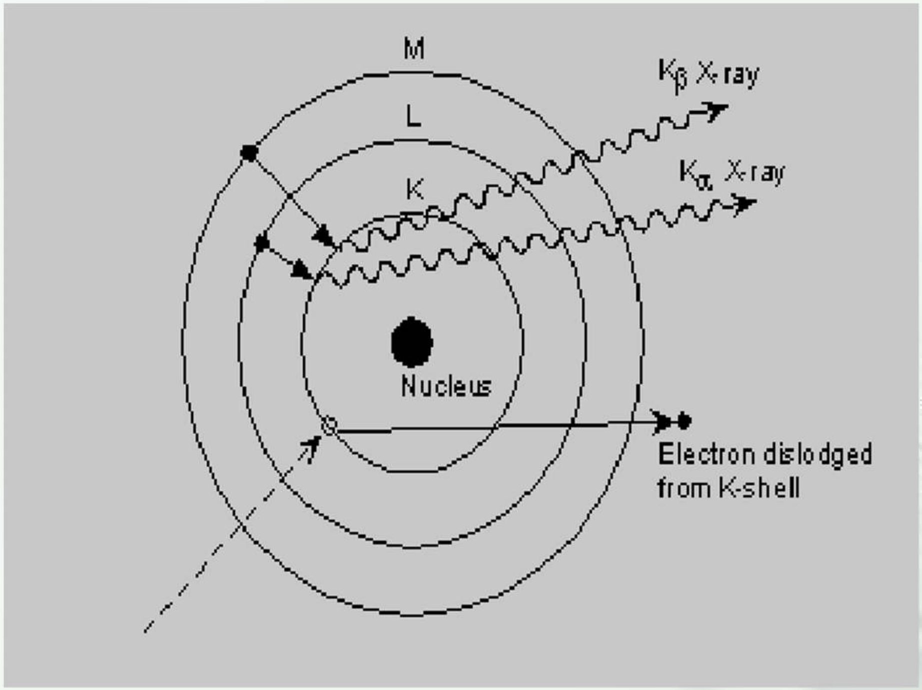
X-ray is produced when electrons hit a target at very high speed. Electrons are circulating around the nucleus of the atom in different orbits with different energies. The farthest layer is M, and to the core are L and K, respectively.

X-Ray Production

If one of the electrons bombing the target (anode) has enough kinetic energy to be able to remove the electron from the K layer, this puts the atom in an excited state and high energy. Immediately when an electron falls from the upper layers such as M or L in the empty space of the K layer, energy is generated and the electron returns to a steady state. The resulting energy is due to the electron falling from the higher energy layer to the lower energy layer.

X-Ray Production

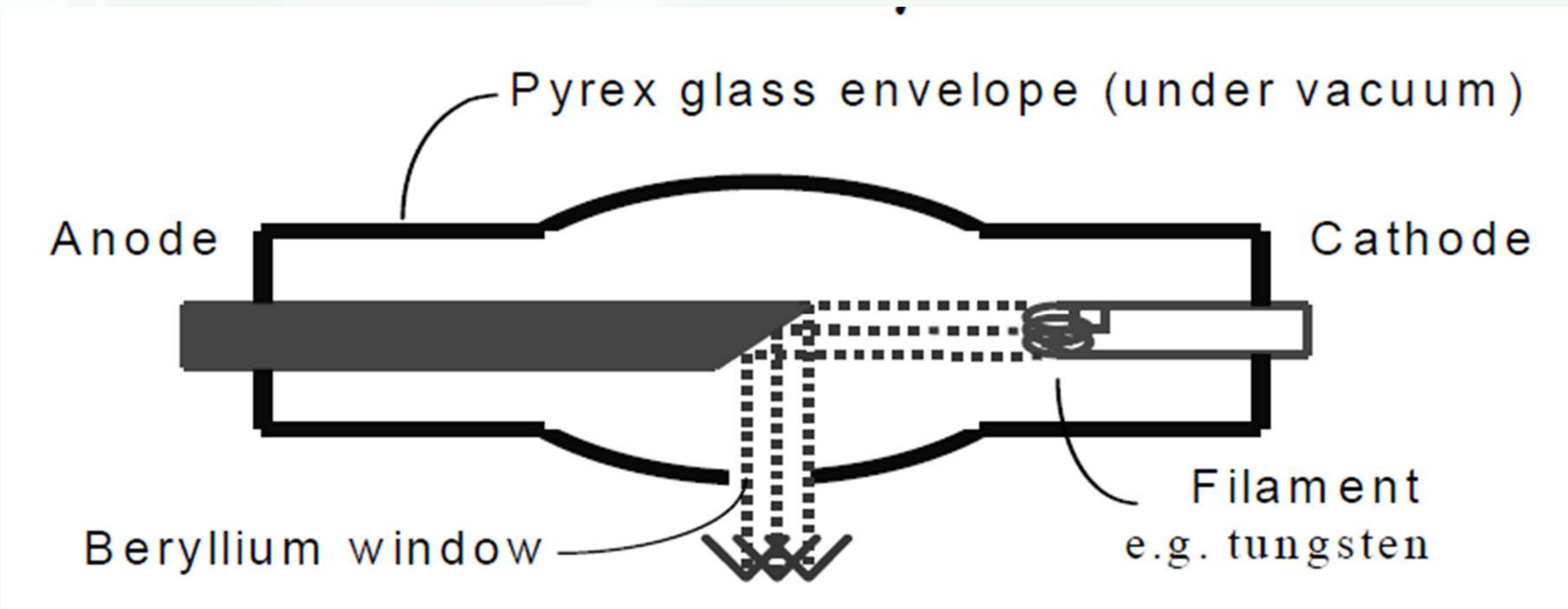
The resulting energy is radiation of a certain wavelength, which in this case is called K radiation. If layer K is filled with electron fall from layer L, the radiation is called Kα, and if it is from layer M, the radiation is called Kβ.



X-Ray Production

An X-ray lamp consists of the following components:

1) Source of electron production (cathode)
2) High voltage generator
3) The anode, which is the target of electrons that hit it at high acceleration.



X-Ray Production

As a result of the electrons hitting the anode, their kinetic energy is converted into heat, so the anode is made of metal (for example Cu) and cooled with water to prevent it from melting.

High voltage is used to accelerate the electrons to strike the anode. The cathode is usually in the form of a filament (Tungsten filament, etc.) which is heated by applying high voltage to emit electrons and move towards the anode due to the potential difference between the cathode and the anode.

X-Ray Filter

X-ray intensities vary at different wavelengths. For example, for copper the amount of $\lambda_{k\alpha}$ is the highest (1.54 angstrom) and as a sharpness on the curve. If we want to have X-rays with a certain wavelength, we have to pass the rays through a filter to get the desired wavelength and weaken the rest of the spectrum.

X-Ray Filter

Different filters with certain thicknesses are used to filter different types of X-rays that are produced with different anodes.

An element suitable for filtering whose atomic number is one unit less than the target atomic number (anode).

Target	Kα (Å)	β-filter	Thickness (μm)	Density (g/cc)	% Kα passed	% Kβ passed
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

X-Ray Crystallography

When X-ray penetrates into the crystal, some of it deflected from its path due to collisions with lattice atoms. The effect of this ray deflected by the crystal can be recorded on the photographic film placed around the crystal. Then, by studying this effect on the film, we can understand the geometric structure of the crystal (unit cell).

X-Ray Crystallography

Each crystal lattice consists of groups of atomic, molecular, or ionic planes of the same shape. Therefore, the reflection of radiation by these planes is done only with certain angles. Because the rays are irradiated to the crystal in the form of parallel waves, the resulting reflections are parallel.

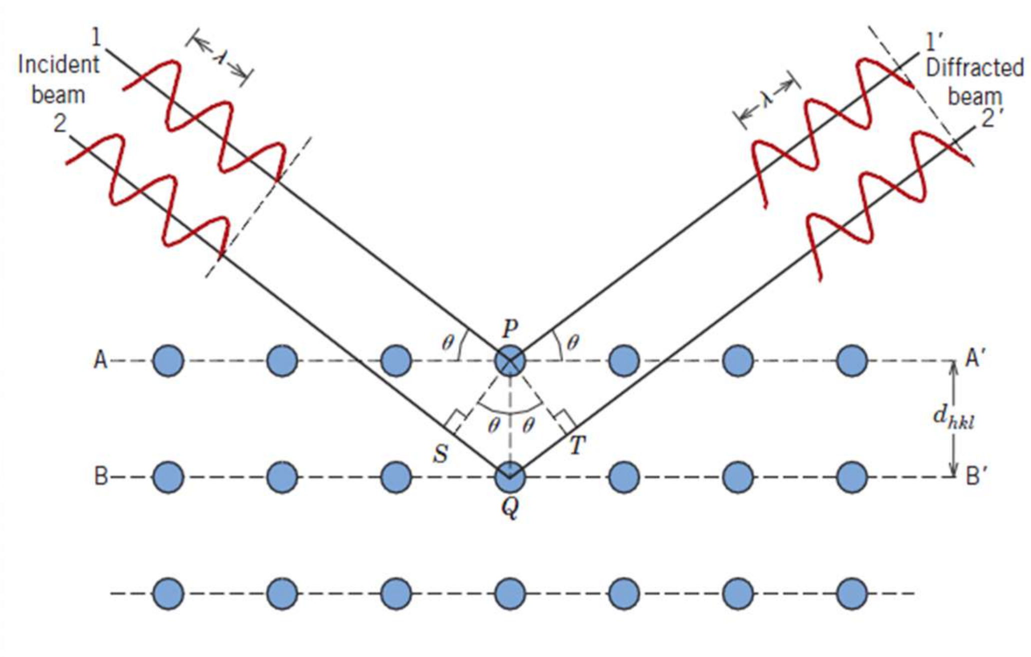
Bragg’s Law

Bragg's law applies to monochromatic X-ray (with specific wavelength). In order for the effect of X-rays on the film to create maximum opacity, it is necessary that the reflected waves are in phase with each other so that the wave resulting from their interference has a great effect (constructive interference).

To cause constructive interference, the path difference between the two rays must be an exact multiple of the wavelength ($n\lambda$).

Bragg's Law

λ: X-ray wavelength
d: Lattice spacing of a crystal structure
n: Diffraction order or degree of reflection (integer)
θ: The angle between the path of a ray and a set of crystal planes (incident angle)



$$n\lambda = d_{hkl}\sin\theta + d_{hkl}\sin\theta$$

$$= 2d_{hkl}\sin\theta$$

In the cubic system we have:

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

a: Axial distance (edge length or lattice parameter) of the cubic crystal
h, k, l: Miller indices of the crystal plane

Bragg's Law

Relation between axial distances (lattice parameters) of crystal lattice and Miller indices of the crystal plane with lattice spacing of a crystal structure

Tetragonal

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$

Hexagonal

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l^2}{c^2}$$

Orthorhombic

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

Rhombohedral

$$\frac{1}{d^2} = \frac{(h^2 + k^2 + l^2)\sin^2\alpha + 2(hk + kl + hl)\cos^2\alpha - \cos\alpha}{a^2(1 - 3\cos^2\alpha + 2\cos^3\alpha)}$$

Bragg's law

Example 1:

For BCC iron, calculate the diffraction angle for the (220) plane. The iron lattice parameter is equal to 0.2866 nm and the monochromatic X-ray wavelength is 0.1790 nm. The diffraction order is considered one.

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

$$= \frac{0.2866 \text{ nm}}{\sqrt{(2)^2 + (2)^2 + (0)^2}} = 0.1013 \text{ nm}$$

$$\sin\theta = \frac{n\lambda}{2d_{hkl}} = \frac{(1)(0.1790 \text{ nm})}{(2)(0.1013 \text{ nm})} = 0.884$$

$$\theta = \sin^{-1}(0.884) = 62.13°$$

The diffraction angle is 2θ, or

$$2\theta = (2)(62.13°) = 124.26°$$

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Allowed Reflections

The relative intensity of different reflections of a crystal depends on the type of crystal structure and the number of atoms in its unit cell.

The atomic arrangement of a crystal can be such that certain crystal planes of that lattice cannot produce the maximum intensity of reflection. In other words, only some planes in each crystal are able to produce the maximum intensity of reflected rays. These planes are called allowed reflection planes.

Allowed Reflection Planes in a Cubic System

- ✓ In the SC (simple cubic) structure, all planes (any hkl) appear:

(100) (110) (111) (200) (210) (211) (220) (221) (300) (310) (311) (222) (320) (321) (400)

- ✓ In the BCC structure, the sum of the indices (hkl) of the planes is even:

(110) (200) (211) (220) (310) (222) (321) (400)

- ✓ In the FCC structure, indices (hkl) of the planes are all even or all odd:

(111) (200) (220) (311) (222) (400)

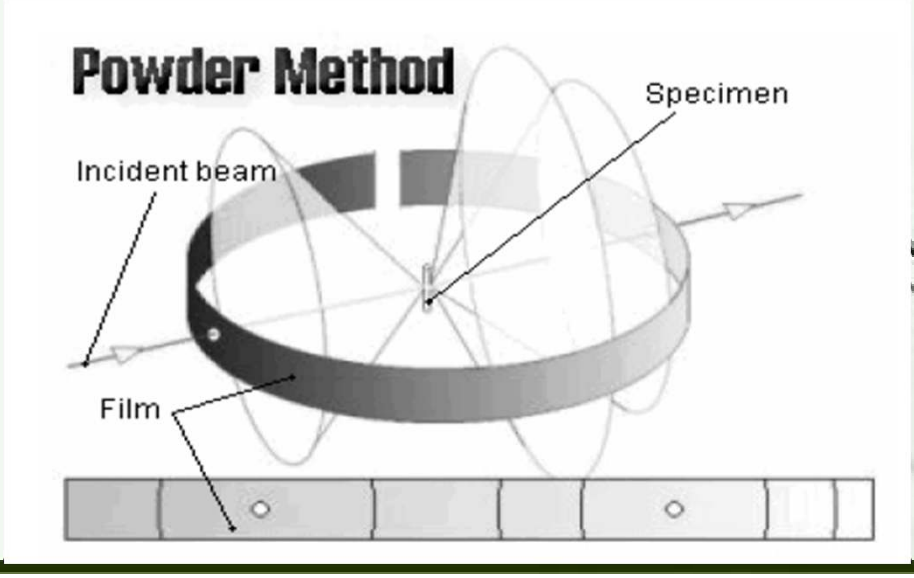
X-Ray Study Methods

There are two general methods for investigating the crystal structure of materials using X-ray diffraction. These methods are based on the X-ray radiation to the sample and studying the effect of the rays deflected by the crystal on the photographic film as follows:

- Debye Scherrer Method: λ is constant and θ is variable.
- Laue Method: λ is variable and θ is constant.

Debye Scherrer Method

In Debye Scherrer method, X-rays with a specific wavelength (monochromatic) are passed through a polycrystalline sample (often in the form of crystalline powder). In this case, the beam is irradiated to a large number of single crystals that are heterogeneously scattered in different directions, and for some of them a Bragg relation is established, and therefore interference lines appear on the film.



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Debye Scherrer Method

All reflected rays make an angle 2θ with the direction of radiation, and the extension of these rays forms a cone with angle 4θ. The diffracted rays in the powder method are placed on the surfaces of several cones that are seen as arcs on the film.

Using the Deby Scherrer method and X-rays with a certain wavelength, the Miller indices of each crystal plane, atomic distances, lattice parameter and also the number of atoms per unit cell of the crystal lattice can be determined.

Debye Scherrer Method

Example 2:

In the study of sodium fluoride crystals using X-rays with a wavelength of 54.1 angstrom, Bragg angles are 31.19, 51.41 and 25.76 degrees. If the unit of crystal lattice is equal to 6342.4 angstroms, determine the distance between ionic planes and identify the planes allowed for reflection.

$$n\lambda = 2dSin\theta \Rightarrow \frac{d}{n} = \frac{\lambda}{2Sin\theta}$$

$$\frac{1.54}{2Sin19.31} = 2.32A$$

$$\frac{1.54}{2Sin41.51} = 1.16A$$

$$\frac{1.54}{2Sin76.25} = 0.791A$$

Debye Scherrer Method

By comparing the resulting numbers for the d/n ratio, it is observed that this ratio for angles 19.31 is twice the angle of 41.51 and it is three times higher than that of 76.25 angle. So, n value is equal to 1, 2 and 3, and as a result:

d = 2.32 A

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \Rightarrow \frac{a}{d} = \frac{4.6342}{2.32} \approx 2 = \sqrt{h^2 + k^2 + l^2}$$

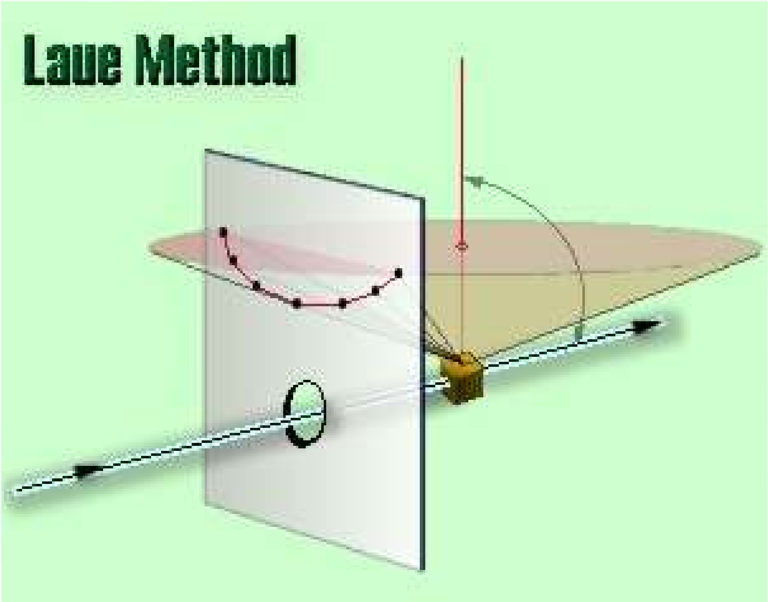
The allowed reflection planes in the FCC crystals are (111), (200), (220), (311), (222) and (400). Therefore, the allowed reflection plane for the given Bragg angles is plane (200) because:

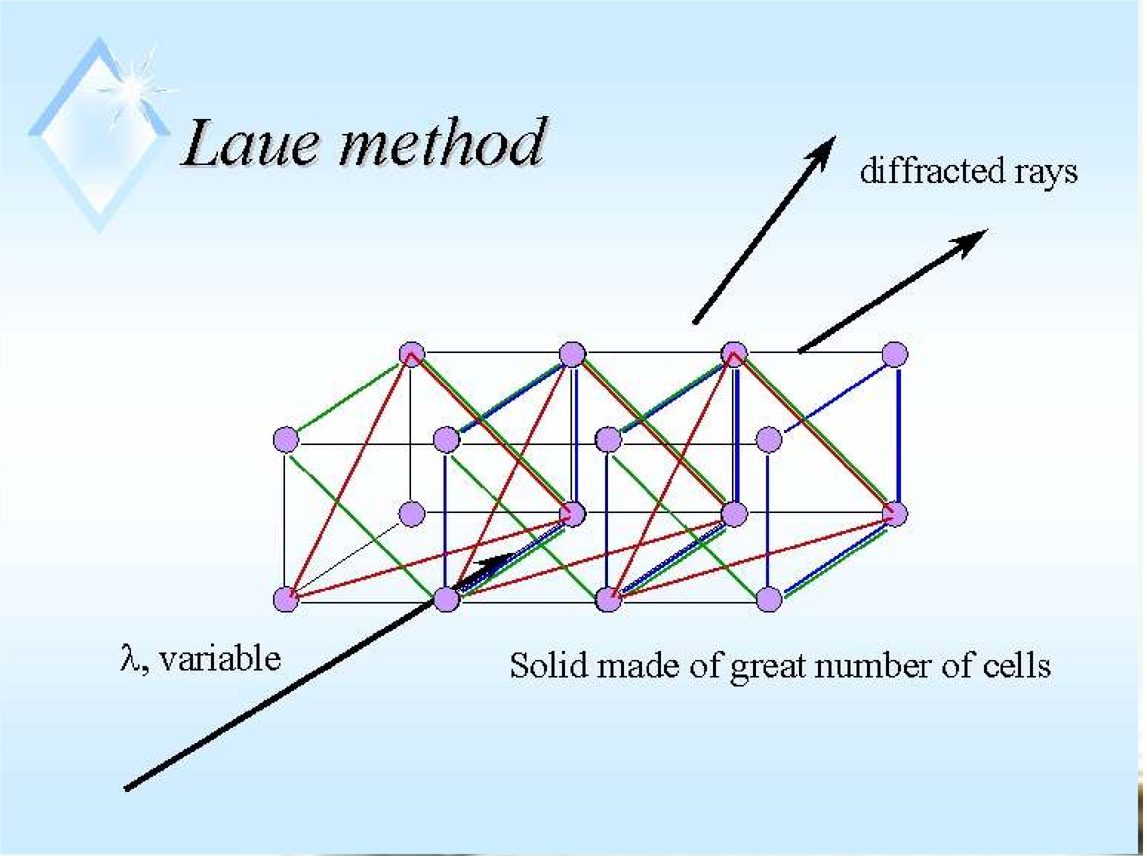
$$\sqrt{h^2 + k^2 + l^2} = \sqrt{2^2 + 0 + 0} = 2$$

Laue Method

In the Laue method, multi-color (polychromatic) X-rays with a wavelength between 0.2- 2 angstrom are used. In this case, too, the radiation on the planes causes scattering and reflection, and for some wavelengths, a Bragg relation is established. The photographic film screen is located behind the sample and therefore several black dots appear in a special order and in the form of a parabola.

Laue Method


Laue Method


Laue method
diffracted rays
λ, variable
Solid made of great number of cells

Laue Method

Example 3:

If white X-rays (with different wavelengths) radiate at an angle of 10 degrees on the (001) plane of an aluminum crystal lattice with a lattice parameter of 4.04 angstrom, what wavelengths are reflected?

$$\lambda_1 = \frac{2 \times 4.04 \sin 10}{1\sqrt{1^2 + 0^2 + 0^2}} = 1.404\,A$$

$$\lambda_2 = \frac{2 \times 4.04 \sin 10}{2\sqrt{1^2 + 0^2 + 0^2}} = 0.702\,A$$

$$\lambda_3 = \frac{2 \times 4.04 \sin 10}{3\sqrt{1^2 + 0^2 + 0^2}} = 0.468\,A$$

$$\lambda_4 = \frac{2 \times 4.04 \sin 10}{4\sqrt{1^2 + 0^2 + 0^2}} = 0.351\,A$$