Determination of crystal structures by X-ray diffraction

Outline

1. Bragg and Von Laue formulation of X-ray diffraction by a crystal
2. Experimental geometries suggested by the Laue condition
3. The geometrical structure factor
4. The atomic form factor

1. Bragg and Von Laue formulation of X-ray diffraction by a crystal
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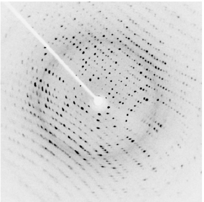
3. The geometrical structure factor
4. The atomic form factor

X-ray diffraction by a crystal

The electromagnetic probe

X-ray diffraction pattern from crystalline solids

- Interatomic distances are of the order of Å (10^{-8}cm)
  - $E = \hbar\omega = \frac{hc}{\lambda} \sim 12.3 \times 10^3$ eV
  - Wavelength and energies characteristic of X-rays
- Exp. observation: sharp peaks of scattered radiation
  - due to long-range order (periodic array of atoms/ions)
  - not found for amorphous solids or liquids (similar density)
- Can reveal the location of the ions in the structure



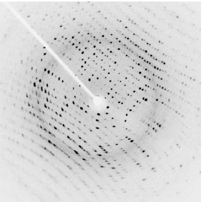
X-ray diffraction pattern from a crystal

X-ray diffraction by a crystal

The electromagnetic probe

X-ray diffraction pattern from crystalline solids

- We consider a rigid lattice of ions
- Effect of vibrations:
  - decrease the intensity of the scattered peaks
  - contribute to a continuos background of diffuse radiation



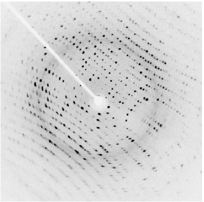
X-ray diffraction pattern from a crystal

X-ray diffraction by a crystal

X-ray diffraction

Scattering of X-ray radiation by a perfect crystal: equivalent formulations

- Bragg formulation
  - used by crystallographers
- Von Laue formulation
  - exploits the reciprocal lattice
  - closer to the solid-state approach



X-ray diffraction pattern from a crystal

X-ray diffraction by a crystal

Bragg formulation

Bragg's interpretation of X-ray diffraction

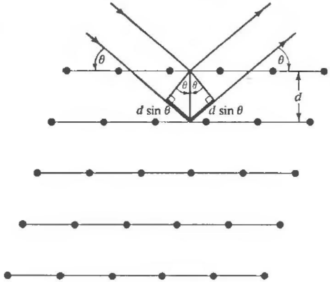
- Crystal composed of parallel planes of ions (family of lattice planes)
  - separated by a distance d
- Conditions for the appearance of sharp diffraction peaks:
  - X-rays are specularly reflected by the ions in the crystal planes
  - constructive interference of reflected X-rays
- Bragg's condition: $2d \sin\theta = n\lambda$
  - n : order of reflection
  - θ: angle of incidence on the crystal's plane
- Many reflections are observed as a result of:
  - X-ray beams containing a range of ν
  - higher-order reflections from a given family of lattice planes
  - many ways of sectioning a crystal into lattice planes

X-ray diffraction by a crystal

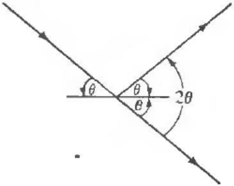
Bragg interpretation of X-ray diffraction

Simple derivation of Bragg condition

- Condition for constructive interference:
  - path difference ($2d \sin \theta$) equals an integral number of wavelengths
  - total angle of deflection of the incident rays: 2θ



reflection from a family of lattice planes



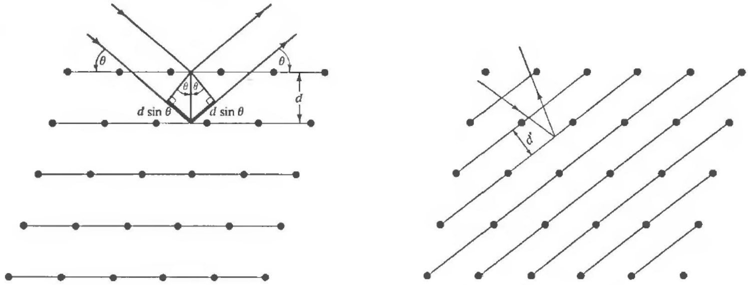
Bragg angle θ

X-ray diffraction by a crystal

Bragg's interpretation of X-ray diffraction

Further observations

- A large number of reflections arise as a result of:
  - X-ray beams containing a range of ν
  - higher-order reflections from a given family of lattice planes
  - many ways of sectioning a crystal into lattice planes



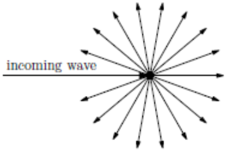
Two possible resolutions of the same crystal lattice into planes

X-ray diffraction by a crystal

Von Laue formulation

Assumptions

- Crystal composed of scatterers at the sites $\boldsymbol{R}$ of a Bravais lattice
  - atoms, ions
- Peaks are observed for directions of constructive interference between all scattered rays
- No particular sectioning of the lattice into crystal planes
- No need to assume specular reflection
  - specular reflection is equivalent to constructive interference btw X-rays scattered from individual atoms of the lattice plane



X-ray diffraction by a crystal

The scattering process

Assumptions of the model

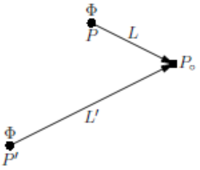
- Diffraction: interaction of light with an obstacle (or slit) that makes the latter to behave as a secondary source of radiation
- We make the following assumptions on the scattering process:
  - the scattering is elastic: λ of the scattered wave is the same of that of the impinging wave
  - the scattering process does not change the phase of the wave (or it changes by a constant amount)
- Interference: wave re-emitted by two (or more) point-like obstacles (slits) separated by a distance $d \sim \lambda$ will interfere giving a diffraction pattern.
  - direct consequence of the superposition principle
- The phase difference btw diffracted waves depends upon the difference in their optical path

X-ray diffraction by a crystal

The scattering process

Constructive and destructive Interference

- Assume two waves with common amplitude A, angular frequency ω, and wavelength λ
  - originating from P and P' (with identical phase), travelling through an observation point P_0
- Optical path difference: $L' - L$
  - constructive interference when $L' = L + n\lambda \longrightarrow a'_{P_0} = a_{P_0}$. Total amplitude is $2a$ at all times
  - destructive interference when $L' = L + (2n+1)\frac{\lambda}{2} \longrightarrow a'_{P_0} = -a_{P_0}$. Total amplitude is 0 at all times



X-ray diffraction by a crystal

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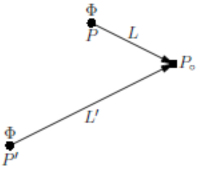
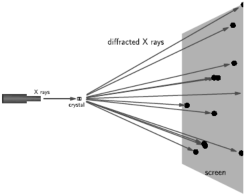


X-ray diffraction by a crystal

Von Laue formulation

X-ray diffraction pattern

- Crystal behaves as a 3D diffraction lattice for the incoming radiation
- Diffracted X-rays will give interference
  - intensity maxima on a detector for directions where constructive interference happens
- Diffracted waves are spherical: approx. plane waves if the point of observation is far away from the scatterers



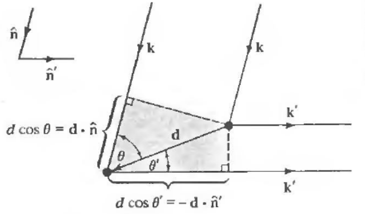
typical diffraction experiment

X-ray diffraction by a crystal

Von Laue formulation

Derivation of the condition of constructive interference

- Wave vector of incident radiation: $\boldsymbol{k} = \frac{2\pi}{\lambda}\hat{\boldsymbol{n}}$
- Wave vector of scattered radiation: $\boldsymbol{k}' = \frac{2\pi}{\lambda}\hat{\boldsymbol{n}}'$
  - assume elastic scattering: $|\boldsymbol{k}'| = |\boldsymbol{k}|$
- Difference in optical path btw interfering waves: $\boldsymbol{d} \cdot (\hat{\boldsymbol{n}} - \hat{\boldsymbol{n}}')$
  - $\boldsymbol{d} \cdot (\boldsymbol{k} - \boldsymbol{k}') = 2\pi m$ (m integer)



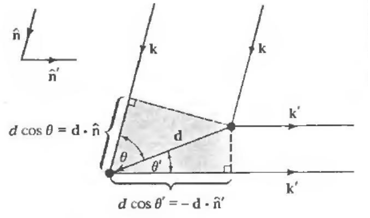
two scattering centers separated by a displacement vector $\boldsymbol{d}$

X-ray diffraction by a crystal

Von Laue formulation

Derivation of the condition of constructive interference

- For all scatteres in the lattice: $\boldsymbol{R} \cdot (\boldsymbol{k} - \boldsymbol{k}') = 2\pi m, \, \forall \, \boldsymbol{R}$
  - all scattered rays interfere constructively
- Alternatively: $e^{i(\boldsymbol{k}'-\boldsymbol{k})\cdot\boldsymbol{R}} = 1$
  - $\boldsymbol{k} - \boldsymbol{k}'$ is a reciprocal lattice vector $\boldsymbol{K}$



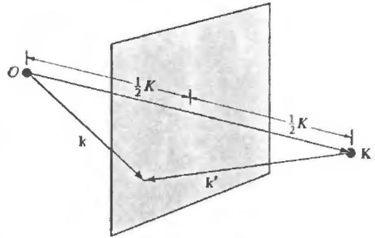
two scattering centers separated by a displacement vector $\boldsymbol{d}$

X-ray diffraction by a crystal

Von Laue formulation

Another geometrical interpretation

- $\boldsymbol{k} - \boldsymbol{k}'$ is a reciprocal lattice vector $\boldsymbol{K}$
- $k = |\boldsymbol{k} - \boldsymbol{K}|$ and squaring
- $\boldsymbol{k} \cdot \hat{\boldsymbol{K}} = \frac{1}{2}K$
    - component of $\boldsymbol{k}$ along $\boldsymbol{K}$



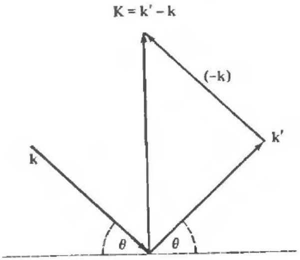
k-space plane (Bragg plane)

X-ray diffraction by a crystal

Equivalence of Bragg and Von Laue formulations

Proof:

- Von Laue condition: $\boldsymbol{k}' - \boldsymbol{k} = \boldsymbol{K}$ $(k' = k)$
- $\boldsymbol{K}$ is $\perp$ to a family of direct lattice planes



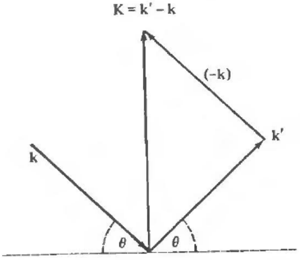
$\boldsymbol{K}$ bisects the angle between $\boldsymbol{k}$ and $\boldsymbol{k}'$

X-ray diffraction by a crystal

Equivalence of Bragg and Von Laue formulations

Proof:

- if d distance between planes, $|\boldsymbol{K}| = 2k\sin\theta = n|\boldsymbol{K}_0| = n\frac{2\pi}{d}$
- $k\sin\theta = \frac{n\pi}{d}$ (Bragg condition)
- Reflection from the family of lattice planes $\perp$ $\boldsymbol{K}$
- Order of reflection is $n = \frac{|\boldsymbol{K}|}{|\boldsymbol{K}_0|}$



$\boldsymbol{K}$ bisects the angle between $\boldsymbol{k}$ and $\boldsymbol{k}'$

Experimental geometries suggested by the Laue condition

The Laue condition

Devising experimental setups

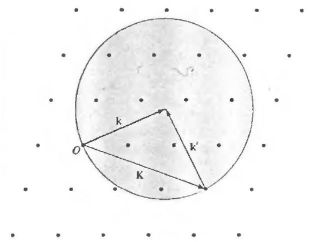
- Laue condition: the tip of $\boldsymbol{k}$ must lie on a Bragg plane
  - k-space plane
  - boundaries (faces) of BZs
- Difficult to realize for fixed orientation of the crystal and fixed λ of X-ray radiation
- How do we achieve enough sampling of the reciprocal space?
  - vary the wavelength of impinging X-rays (magnitude of $\boldsymbol{k}$)
  - vary the direction of incidence (i.e. relative orientation of the crystal)
- Simple geometrical construction to visualize experimental techniques: the Ewald construction

Experimental geometries suggested by the Laue condition

A geometrical construction

The Ewald sphere

- Draw a sphere of radius k centered on the tip of $\boldsymbol{k}$ ($k = \frac{2\pi}{\lambda}$)
  - passes through the origin of $\mathcal{R}^*$
- Diffraction peaks for reciprocal lattice points on the surface of the sphere
  - $\boldsymbol{k}'$ satisfies the Laue condition

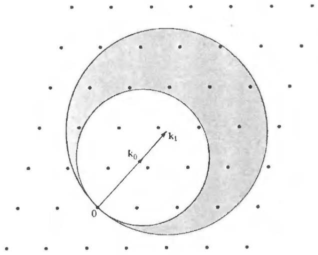


the Ewald construction

Experimental geometries suggested by the Laue condition

The Laue method

- Use polychromatic X-rays (from λ_1 to λ_0)
  - fixed orientation of the crystal and incident direction $\hat{\boldsymbol{n}}$
  - $\boldsymbol{k}_1 = \frac{2\pi}{\lambda_1}\hat{\boldsymbol{n}}$, $\boldsymbol{k}_0 = \frac{2\pi}{\lambda_0}\hat{\boldsymbol{n}}$
- Diffracted rays in correspondence to multiple reciprocal lattice points
  - included in the 3D region between the two spheres of radii k_0 and k_1
- Better used for determining the orientation of a single crystal of known structure



the Ewald construction for the Laue method

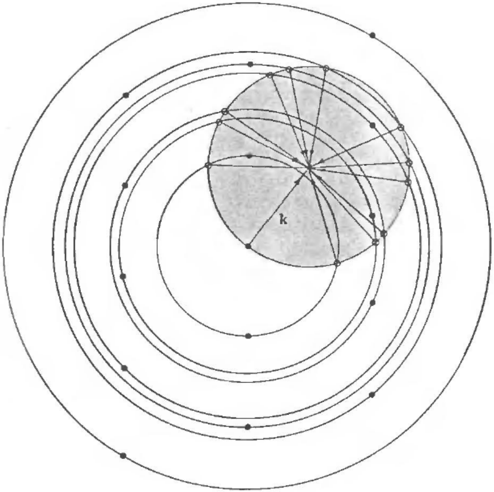
Experimental geometries suggested by the Laue condition

The rotating-crystal method

- Use monochromatic X-rays of fixed incident direction
- Vary the orientation of the crystal
  - Rotation around a fixed axis: the reciprocal lattice rotates around the same axis by the same amount
- The Ewald sphere is fixed in k-space
- Each reciprocal lattice point traverses a circle about the axis of rotation
- Bragg reflection when the circle intersects the Ewald sphere

Experimental geometries suggested by the Laue condition

The rotating-crystal method



the Ewald construction for the rotating-crystal method

Experimental geometries suggested by the Laue condition

The Debye-Scherrer Method

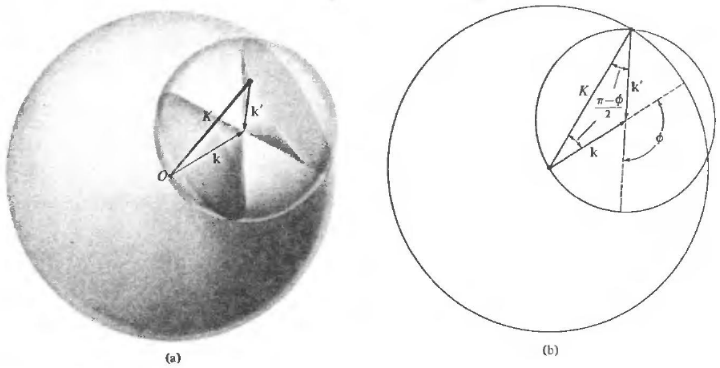
Powder Method

- Equivalent ot the rotating-crystal method with rotation axis varied over all possible directions
  - isotropic averaging of the incident direction
- Experimentally achieved by using a polycristalline sample or finely dispersed powder
  - crystal axes of the individual grains are randomly oriented
- Incident wave vector $\boldsymbol{k}$ and Ewald sphere are fixed
- The reciprocal lattice rotates through all possible angles about the origin
  - each $\boldsymbol{K}$ generates a sphere of radius K
  - intersect the Ewald sphere in a circle
- All $\boldsymbol{K}$ such that $K < 2k$ generates a cone of diffracted radiation at an angle ϕ in the forward direction
  - $K = 2k \sin \frac{1}{2}\phi$

Experimental geometries suggested by the Laue condition

The Debye-Scherrer Method

Powder Method



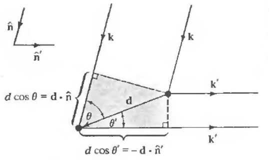
the Ewald construction for the Debye-Scherrer Method

Diffraction by a monoatomic lattice with a basis

The geometrical structure factor

Several identical scatterers in the primitive cell

- n scatterers at positions $\{\boldsymbol{d}_i\}_{i=1,\dots,n}$
  - Bravais lattice with a n-atom basis
  - e.g. diamond structure: FCC lattice with $n=2$
- For a Bragg peak with $\boldsymbol{K} = \boldsymbol{k}' - \boldsymbol{k}$
  - intensity of the peak will depend on constructive/desctructive interference btw scattered rays from the basis sites
  - phase difference btw waves scattered at $\boldsymbol{d}_i$ and $\boldsymbol{d}_j$: $\boldsymbol{K} \cdot (\boldsymbol{d}_i - \boldsymbol{d}_j)$



path difference btw rays scattered by centers at a distance $\boldsymbol{d}$

Diffraction by a monoatomic lattice with a basis

The geometrical structure factor

Several identical scatterers in the primitive cell

- The amplitude of the rays will differ by a factor $e^{i\boldsymbol{K}\cdot(\boldsymbol{d}_i-\boldsymbol{d}_j)}$
- For the n scatterers at positions $\{\boldsymbol{d}_i\}_{i=1,\dots,n}$, the amplitudes are in the ratio:

$$e^{i\boldsymbol{K}\cdot\boldsymbol{d}_1} : e^{i\boldsymbol{K}\cdot\boldsymbol{d}_2} : \dots e^{i\boldsymbol{K}\cdot\boldsymbol{d}_n}$$

- The total amplitude of X-ray scattered by the cell contains the factor:

$$S_{\boldsymbol{K}} = \sum_{j=1}^{n} e^{i\boldsymbol{K}\cdot\boldsymbol{d}_j}$$

- $S_{\boldsymbol{K}}$: geometrical structure factor
- amount to which the interference of the waves scattered by indentical ions within the basis can diminish the intensity of the Bragg peak associated with $\boldsymbol{K}$

Diffraction by a monoatomic lattice with a basis

The geometrical structure factor

Absolute intensity in a Bragg peak

- The intensity depends on $\boldsymbol{K}$ through $S_{\boldsymbol{K}}$: $I_{\boldsymbol{K}} \propto |S_{\boldsymbol{K}}|^2$
- Not the only source of $\boldsymbol{K}$ dependence
  - characteristic angular dependence of the scattering process
  - details of the internal structure of the scatterer
- $S_{\boldsymbol{K}}$ alone cannot be used to predict the absolute intensity of a Bragg peak
- However, when $S_{\boldsymbol{K}} = 0 \Longrightarrow I_{\boldsymbol{K}} = 0$
  - complete destructive interference for the $\boldsymbol{K}$ in question

Vanishing structure factor

Examples

bcc viewed as a sc lattice with a basis

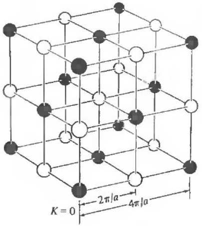
- The reciprocal lattice is fcc
- bcc can be regarded as a sc lattice with a basis
  - primitive vectors: $a\hat{\boldsymbol{x}}$, $a\hat{\boldsymbol{y}}$, $a\hat{\boldsymbol{z}}$
  - basis: $\boldsymbol{d}_1 = 0$, $\boldsymbol{d}_2 = (\frac{a}{2})(\hat{\boldsymbol{x}} + \hat{\boldsymbol{y}} + \hat{\boldsymbol{z}})$
- $\boldsymbol{K}$ must be a vector of the reciprocal lattice
  - $\boldsymbol{K} = \frac{2\pi}{a}(n_1\hat{\boldsymbol{x}} + n_2\hat{\boldsymbol{y}} + n_3\hat{\boldsymbol{z}})$
- $S_{\boldsymbol{K}} = 1 + e^{i\pi(n_1+n_2+n_3)} = 1 + (-1)^{n_1+n_2+n_3}$
  - $S_{\boldsymbol{K}} = 2$ when $n_1 + n_2 + n_3$ is even
  - $S_{\boldsymbol{K}} = 0$ when $n_1 + n_2 + n_3$ is odd

Vanishing structure factor

Examples

bcc viewed as a sc lattice with a basis

- $\boldsymbol{K}$ vectors for which $S_{\boldsymbol{K}} = 0$ will have no Bragg reflection
  - odd number of nearest-neighbour bonds from the origin
- $\boldsymbol{K}$ vectors for which $S_{\boldsymbol{K}} \neq 0$ define a reciprocal fcc lattice with a cubic cell with lattice parameter $a^* = \frac{4\pi}{a}$
  - the reciprocal lattice that we would have had for the bcc direct lattice



$\boldsymbol{K}$ points for which $S_{\boldsymbol{K}} = 2$ (black circles) and $S_{\boldsymbol{K}} = 0$ (white circles)

Vanishing structure factor

Examples

Monoatomic diamond lattice (C, Si, Ge, grey tin)

- Not a Bravais lattice
- Viewed as a fcc lattice with a two-atom basis
  - $\boldsymbol{a}_1 = \frac{a}{2}(\hat{\boldsymbol{y}} + \hat{\boldsymbol{z}})$; $\boldsymbol{a}_2 = \frac{a}{2}(\hat{\boldsymbol{x}} + \hat{\boldsymbol{z}})$; $\boldsymbol{a}_3 = \frac{a}{2}(\hat{\boldsymbol{x}} + \hat{\boldsymbol{y}})$
  - two point basis: $\boldsymbol{d}_1 = 0$, $\boldsymbol{d}_2 = \frac{a}{4}(\hat{\boldsymbol{x}} + \hat{\boldsymbol{y}} + \hat{\boldsymbol{z}})$
- $\boldsymbol{K}$ must be a vector of the bcc reciprocal lattice: $\boldsymbol{K} = \sum_i n_i \boldsymbol{b}_i$
  - cubic cell of side of $\frac{4\pi}{a}$
  - $\boldsymbol{b}_1 = \frac{2\pi}{a}(\hat{\boldsymbol{y}} + \hat{\boldsymbol{z}} - \hat{\boldsymbol{x}})$; $\boldsymbol{b}_2 = \frac{2\pi}{a}(\hat{\boldsymbol{x}} + \hat{\boldsymbol{z}} - \hat{\boldsymbol{y}})$; $\boldsymbol{b}_3 = \frac{2\pi}{a}(\hat{\boldsymbol{x}} + \hat{\boldsymbol{y}} - \hat{\boldsymbol{z}})$
- $S_{\boldsymbol{K}} = 1 + e^{i\frac{\pi}{2}(n_1+n_2+n_3)}$
  - $S_{\boldsymbol{K}} = 2$ when $n_1 + n_2 + n_3$ is twice an even number
  - $S_{\boldsymbol{K}} = 0$ when $n_1 + n_2 + n_3$ is twice an odd number
  - $S_{\boldsymbol{K}} = 1 \pm i$ when $n_1 + n_2 + n_3$ is odd

Vanishing structure factor

Examples

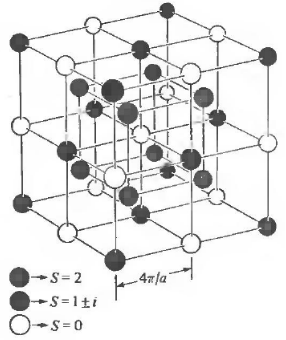
Monoatomic diamond lattice (C, Si, Ge, grey tin)

- $\boldsymbol{K} = \sum_i n_i \boldsymbol{b}_i = \frac{4\pi}{a}(\nu_1 \hat{\boldsymbol{x}} + \nu_2 \hat{\boldsymbol{y}} + \nu_3 \hat{\boldsymbol{z}})$
  - $\nu_j = \frac{1}{2}(n_1 + n_2 + n_3) - n_j$
  - $\sum_j \nu_j = \frac{1}{2}(n_1 + n_2 + n_3)$
- The bcc Bravais lattice is viewed as composed of two sc Bravais lattices of sides $\frac{4\pi}{a}$
- One contains the origin ($\boldsymbol{K} = 0$):
  - ν_i are integers ($n_1 + n_2 + n_3$ twice an even/odd)
  - $S_{\boldsymbol{K}} = 0, 2$ ($S_{\boldsymbol{K}} = 0$ when $\sum_j \nu_j$ is odd, as before)
  - converts the sc lattice into a fcc lattice
- The other contains $\boldsymbol{K} = \frac{4\pi}{a}\frac{1}{2}(\hat{\boldsymbol{x}} + \hat{\boldsymbol{y}} + \hat{\boldsymbol{z}})$
  - all ν_i must be integer $+\frac{1}{2} \longrightarrow n_1 + n_2 + n_3$ odd
  - $S_{\boldsymbol{K}} = 1 \pm i$

Vanishing structure factor

Examples

Monoatomic diamond lattice (C, Si, Ge, grey tin)



$\boldsymbol{K}$ points for which $S_{\boldsymbol{K}} = 2$, $S_{\boldsymbol{K}} = 1 \pm i$, and $S_{\boldsymbol{K}} = 0$ (white circles)

Diffraction by a polyatomic crystal

The atomic form factor

Scattering by different centers in the basis

- If the scatterers are not identical:

$$S_{\boldsymbol{K}} = \sum_{j=1}^{n} f_j(\boldsymbol{K}) e^{i\boldsymbol{K}\cdot\boldsymbol{d}_j}$$

  - $f_j(\boldsymbol{K})$: atomic form factor
  - $f_j(\boldsymbol{K})$ depends on the internal structure of the atom/ion at position $\boldsymbol{d}_j$ in the primitive cell
- Identical centers have the same $f_j(\boldsymbol{K})$
- When all scatterers in the primitive cell are the same:

$$S_{\boldsymbol{K}} = f(\boldsymbol{K}) \sum_{j=1}^{n} e^{i\boldsymbol{K}\cdot\boldsymbol{d}_j}$$

Diffraction by a polyatomic crystal

The atomic form factor

Scattering by different centers in the basis

- In simple treatments:

$$f_j(\boldsymbol{K}) = -\frac{1}{e}\int d\boldsymbol{r}\, e^{i\boldsymbol{K}\cdot\boldsymbol{r}}\rho_j(\boldsymbol{r})$$

  - Fourier transform of the electron density $\rho_j(\boldsymbol{r})$ ($f_j(\boldsymbol{K})$ is dimensionless)
  - $\rho_j(\boldsymbol{r})$: electronic charge density of ion of type j at $\boldsymbol{r} = 0$
  - structure factor usually not vanishing for any $\boldsymbol{K}$
- Our treatment of X-ray diffraction used only the wave properties of X-ray
- Concepts and results can be applied in discussing other wave like phenomena such as those related to electrons, neutrons, etc.