

The Structure Amplitude:

$$\mathbf{F}(\mathbf{h}) = \sum_{j=1}^n g^j t^j(s) f^j(s) \exp(2\pi i \mathbf{h} \cdot \mathbf{x}^j) \quad \text{Eq. 9.1}$$

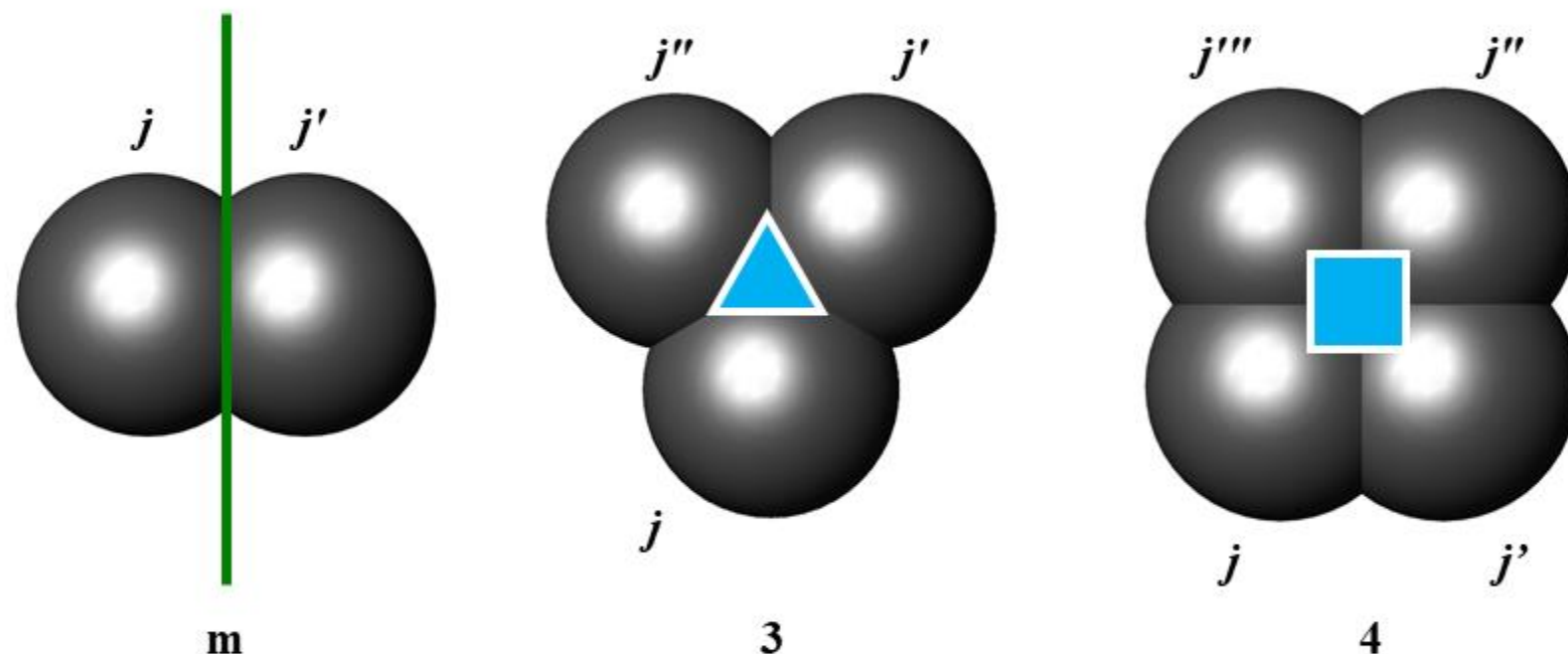
where:

- $\mathbf{F}(\mathbf{h})$ is the structure amplitude of a Bragg reflection with indices hkl , represented as the vector $\mathbf{h}$;
- n is the total number of atoms in the unit cell;
- s is $\sin \theta_{hkl} / \lambda$;
- g^j is the **population** (or occupation) **factor** of the j^{th} atom ($g^j = 1$ for a fully occupied site);
- t^j is the **temperature factor**, which describes the thermal motions of the j^{th} atom;
- $f^j(s)$ is the **atomic scattering factor**, which a function of $\sin \theta / \lambda$ for X-rays and constant for neutrons;
- $i = \sqrt{-1}$;
- $\mathbf{h} \cdot \mathbf{x}^j$ is a scalar product of two vectors: $\mathbf{h} = (h, k, l)$ and $\mathbf{x}^j = (x^j, y^j, z^j)$.

$$\mathbf{h} \cdot \mathbf{x}^j = \begin{pmatrix} h & k & l \end{pmatrix} \times \begin{pmatrix} x^j \\ y^j \\ z^j \end{pmatrix} = hx^j + ky^j + lz^j \quad \text{Eq. 9.2}$$



The Population (or Occupation) Factor:



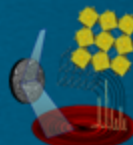
$$g^0 + \sum_{j=1}^m g^j = 1 \quad \text{Eq. 9.4}$$

Where:

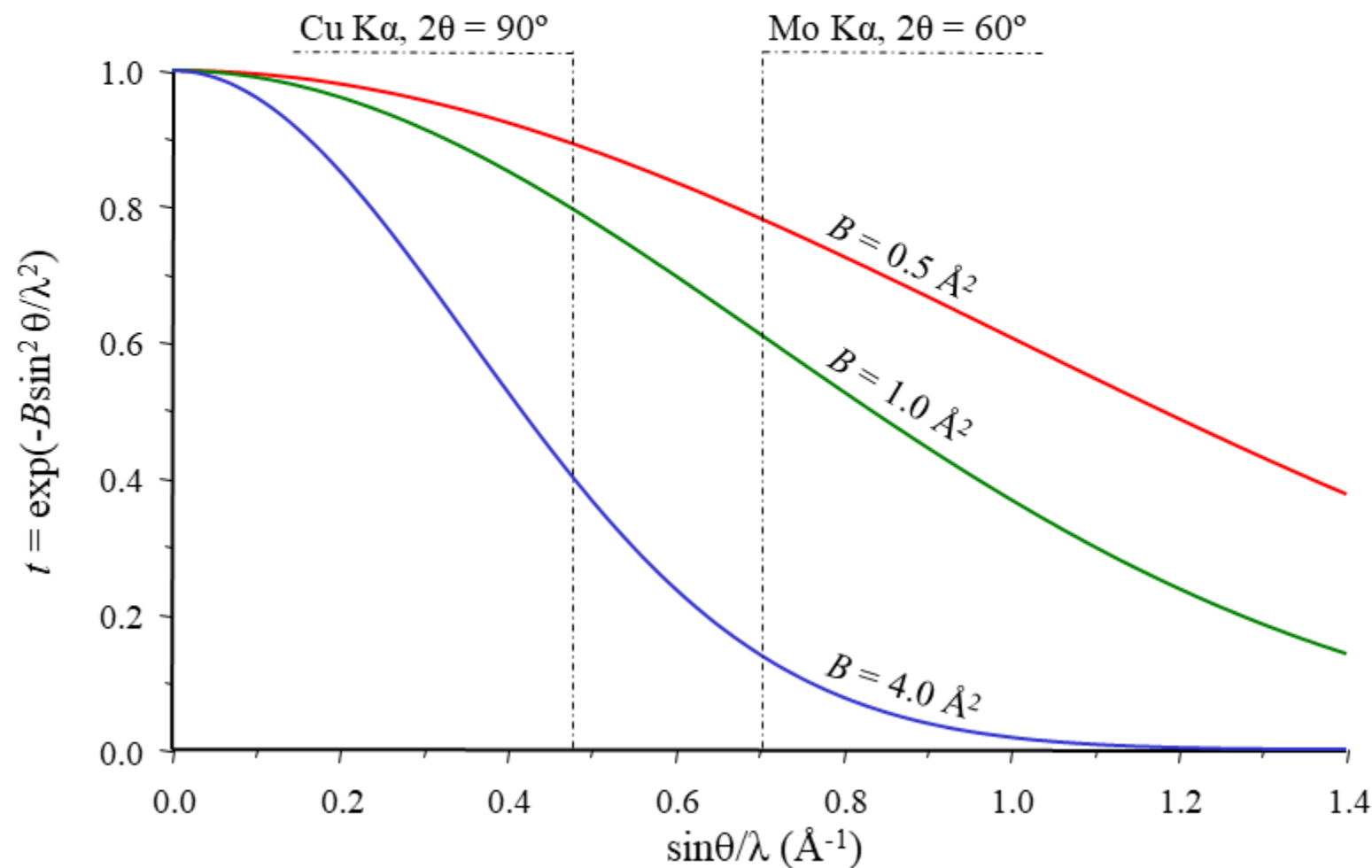
- g^0 represents the unoccupied fraction of the unit cells (defect),
- m is the number of different types of atoms that occupy a given site position in different unit cells.

For this example, $g^0=0$ and $m = 2, 3$ and 4 for **m**, **3** and **4** respectively.

Figure 9.1. The illustration of forbidden overlaps resulting from an atom being too close to a finite symmetry element: mirror plane (*left*), three-fold rotation axis (*middle*), and four-fold rotation axis (*right*).



The Temperature Factor:



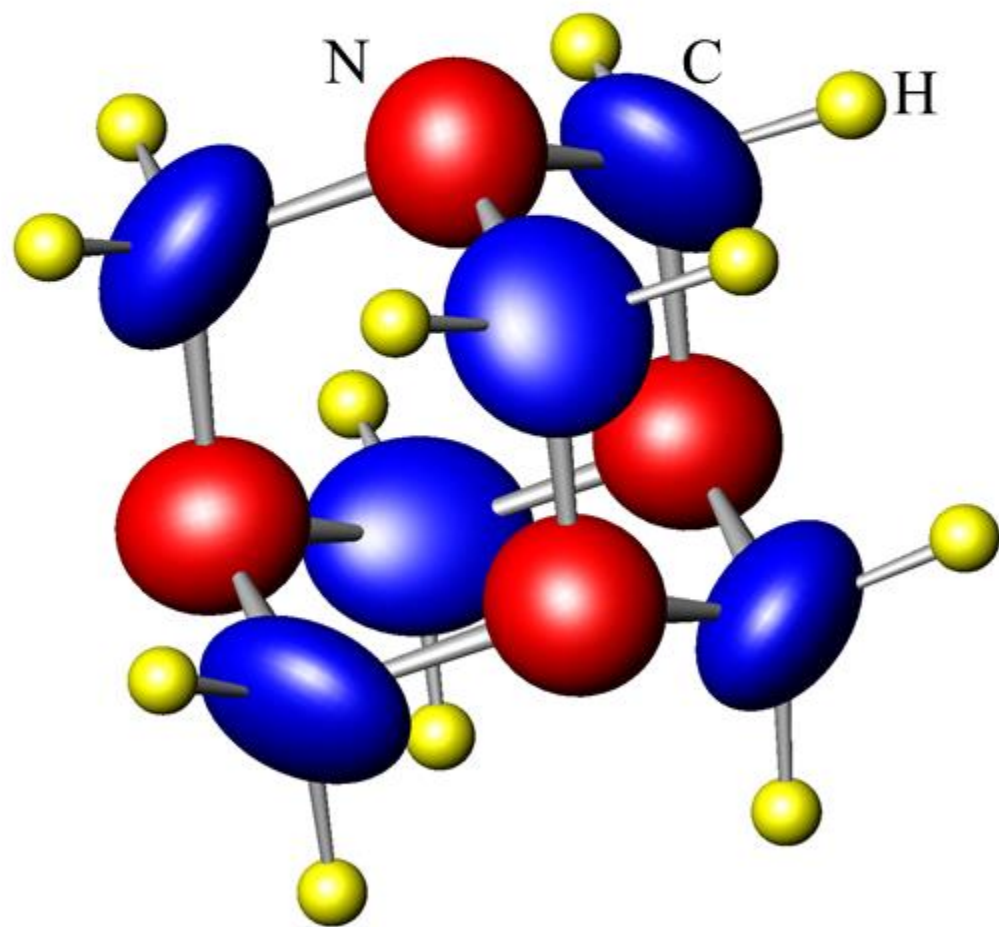
$$t^j = \exp\left(-B^j \frac{\sin^2 \theta}{\lambda^2}\right) \quad \text{Eq. 9.5}$$

$$B^j = 8\pi^2 (\bar{u}^2)^j \quad \text{Eq. 9.6}$$

Figure 9.2. Temperature factor as a function of $\sin \theta / \lambda$ for several different atomic displacement parameters: $B = 0.5, 1.0$, and $4.0 \text{ \AA}^2$. The two vertical *dash-dotted lines* correspond to two commonly employed upper limits of the Bragg angle in diffraction experiments using CuK α and MoK α radiation.



The Anisotropic Temperature Factor:



$$t^j = \exp\left[-\frac{1}{4}(B_{11}^j h^2 a^{*2} + B_{22}^j k^2 b^{*2} + B_{33}^j l^2 c^{*2} + 2B_{12}^j hka^*b^* + 2B_{13}^j hla^*c^* + 2B_{23}^j klb^*c^*)\right] \quad \text{Eq. 9.8}$$

$$B_{ii} > 0$$

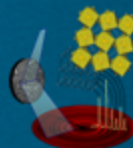
$$B_{ii}B_{ij} > B_{ij}^2$$

$$B_{11}B_{22}B_{33} + B_{12}^2B_{13}^2B_{23}^2$$

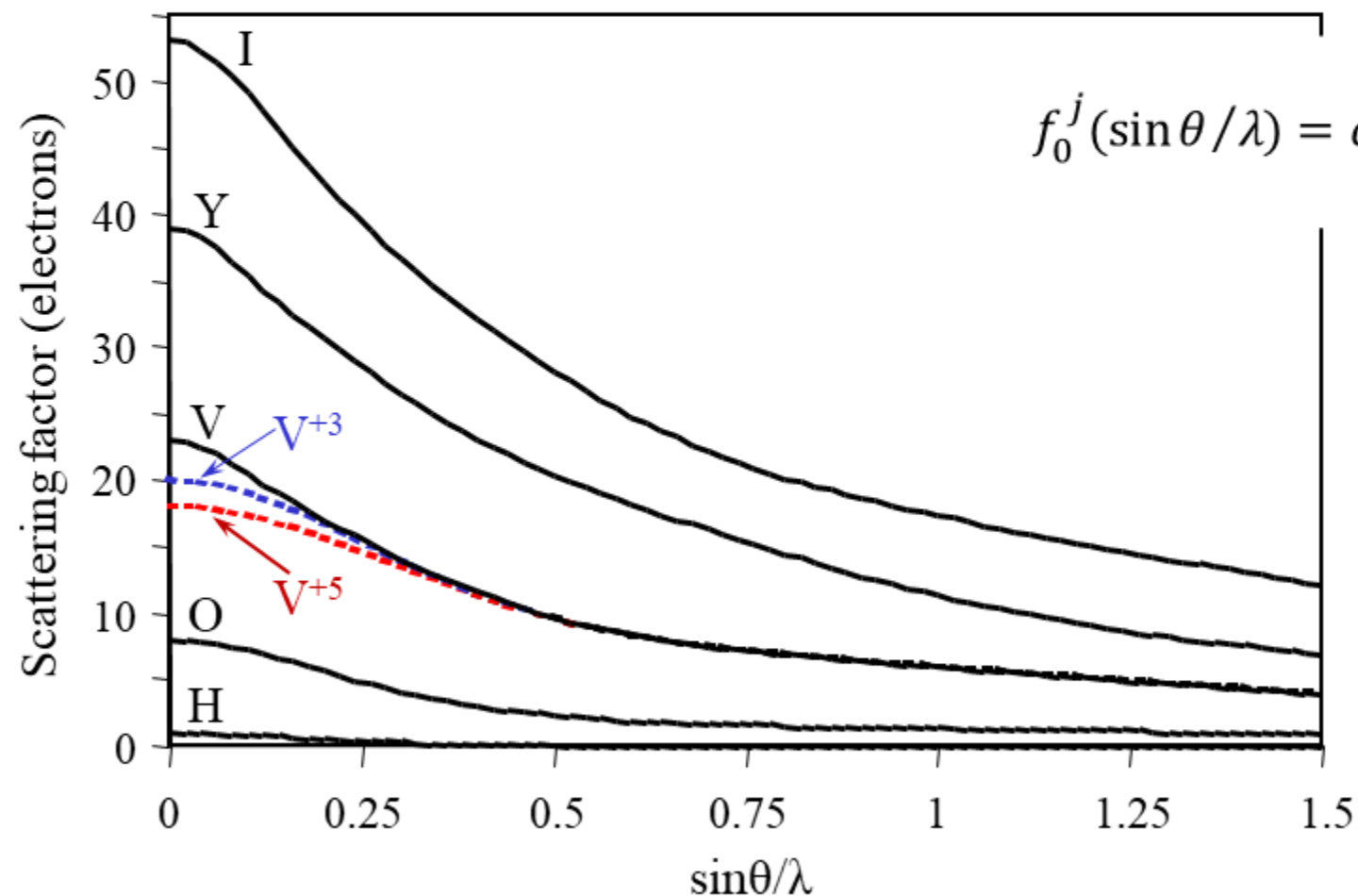
$$> B_{11}B_{23}^2 + B_{22}B_{13}^2 + B_{33}B_{12}^2$$

Eq. 9.11

Figure 9.3. The atomic displacement ellipsoids of carbon and nitrogen atoms shown at the 50 % probability level for the hexamethylenetetramine molecule, as determined from powder diffraction data (see problem 5 on page 667). Hydrogen atoms were refined in the isotropic approximation (Eq. 9.5) and are shown as small spheres of an arbitrary radius.

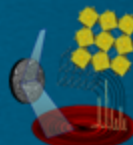


The Atomic Scattering Factor:



$$f_0^j(\sin\theta/\lambda) = c_0^j + \sum_{i=1}^4 a_i^j \exp(-b_i^j \sin\theta/\lambda) \quad \text{Eq. 9.14}$$

Figure 9.4. Atomic scattering factors of H, O, V^{+5} , V^{+3} , V, Y and I as functions of $\sin\theta/\lambda$, appearing in order from the bottom to the top. The scattering factors of vanadium ions become nearly identical to that of the neutral atom at $\sin\theta/\lambda \geq 0.25$, which corresponds to $2\theta \geq 45^\circ$ (Cu $K\alpha$).



The Anomalous Scattering Factor:

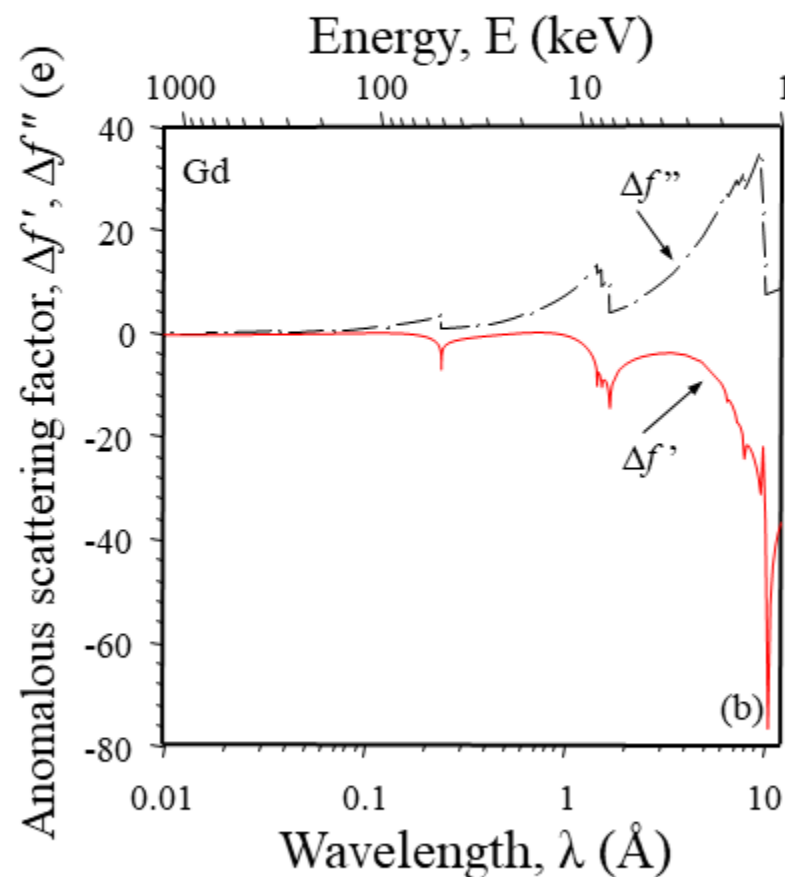
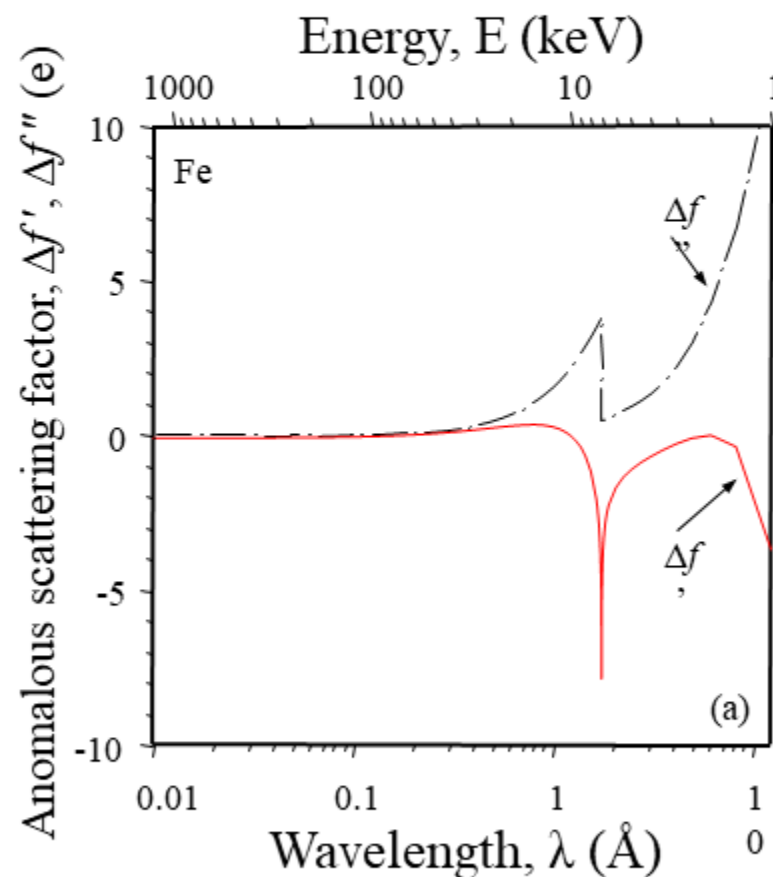
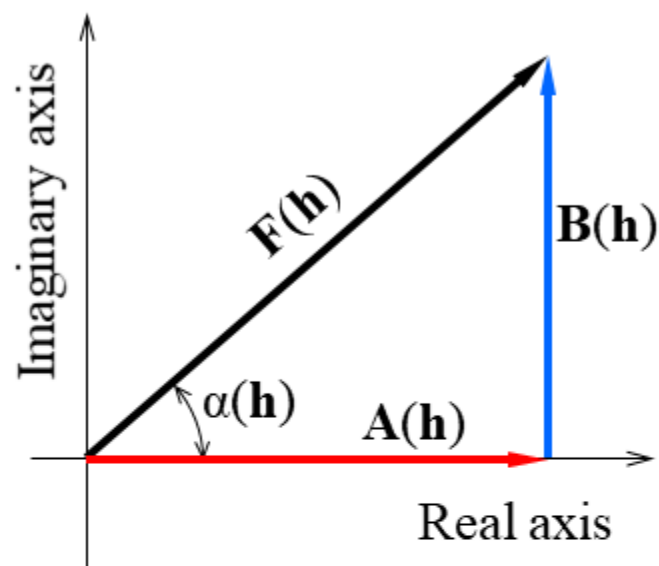
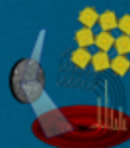


Figure 9.5. Anomalous scattering factors, $\Delta f'$ and $\Delta f''$, of Fe and Gd as functions of wavelength (bottom scale) and photon energy (upper scale).

Eq. 9.15

$$f^j(s) = f_0^j(s) + \Delta f^{j'} + i\Delta f^{j''}$$



$$e^{ix} = \cos x + i \sin x$$

Eq. 9.16

$$F_{hkl} = \sum_{j=1}^n g^j t^j(s) f^j(s) \cos[2\pi(hx^j + ky^j + lz^j)] + i \sum_{j=1}^n g^j t^j(s) f^j(s) \sin[2\pi(hx^j + ky^j + lz^j)]$$

Eq. 9.17

$$\mathbf{F}(\mathbf{h}) = \mathbf{A}(\mathbf{h}) + i\mathbf{B}(\mathbf{h})$$

Eq. 9.18

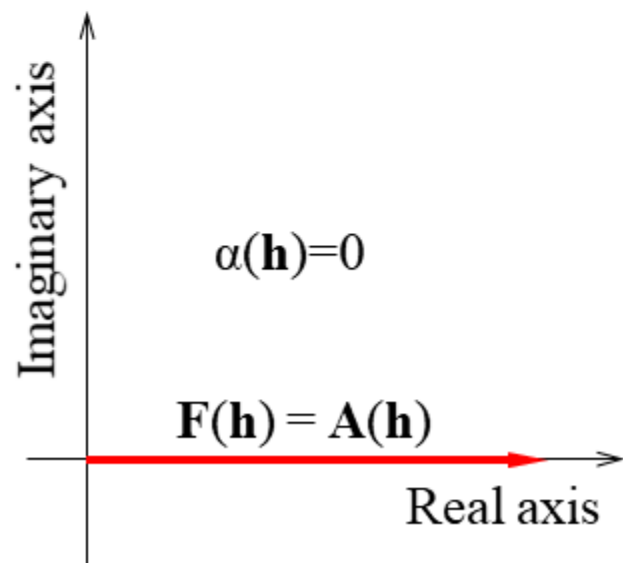
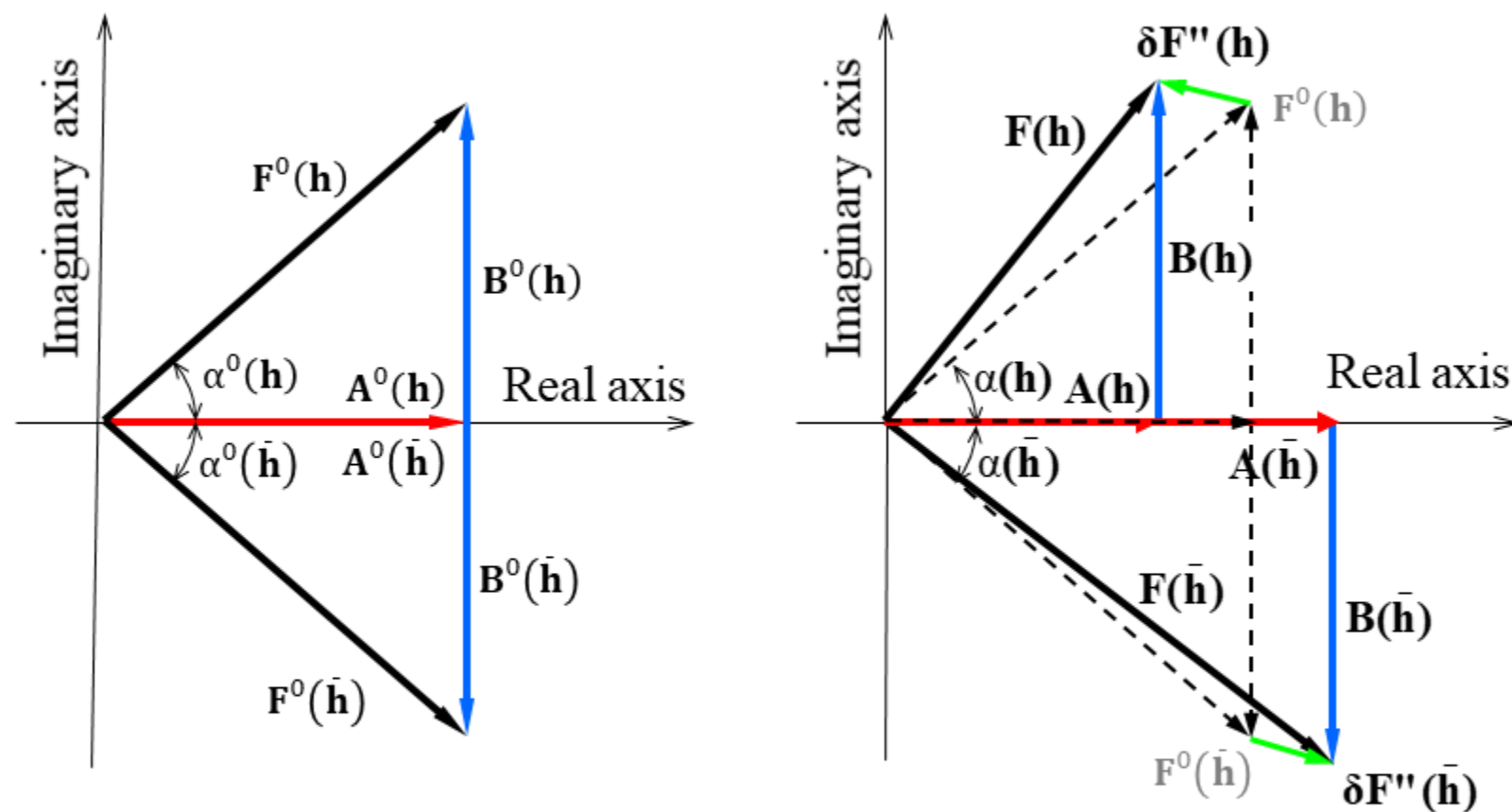
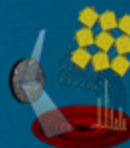


Figure 9.6. The structure amplitude, $\mathbf{F}(\mathbf{h})$, shown as a vector representing a complex number with its real, $\mathbf{A}(\mathbf{h})$, and imaginary, $\mathbf{B}(\mathbf{h})$, components as projections on the real and imaginary axes, respectively, in the non-centrosymmetric (*upper*) and centrosymmetric (*lower*) structures. The imaginary component on the left is shifted from the origin of coordinates for clarity.



Eq. 9.30

$$A(\mathbf{h}) = A^0(\mathbf{h}) + \delta A''(\mathbf{h})$$

$$A(\bar{\mathbf{h}}) = A^0(\mathbf{h}) - \delta A''(\mathbf{h})$$

$$B(\mathbf{h}) = B^0(\mathbf{h}) + \delta B''(\mathbf{h})$$

$$B(\bar{\mathbf{h}}) = -B^0(\mathbf{h}) + \delta B''(\mathbf{h})$$

Eq. 9.19

$$\alpha(\mathbf{h}) = \arctan \left(\frac{|B(\mathbf{h})|}{|A(\mathbf{h})|} \right)$$

Figure 9.7. The relationships between different components of the structure amplitude in a Friedel pair are shown for two cases: when all atoms scatter normally (*left*) and when anomalously scattering atoms are present in the crystal structure (*right*), assuming

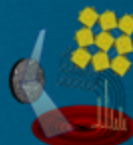


$$I(h) \approx |F(h)|^2 = (A^\circ + \delta A'')^2 + (B^\circ + \delta B'')^2$$

Eq. 9.31

$$I(\bar{h}) \approx |F(\bar{h})|^2 = (A^\circ - \delta A'')^2 + (-B^\circ + \delta B'')^2$$

Therefore, $I(h) \neq I(\bar{h})$ and $|F(h)|^2 \neq |F(\bar{h})|^2$ indicating that Friedel's law is violated in non-centrosymmetric crystal structures containing anomalously scattering atoms. We leave it to the reader to determine the difference $|F(h)|^2 - |F(\bar{h})|^2$ as a function of A° , B° , $\delta A''$, and $\delta B''$ using Eq. 9.31.

**Table 9.1.** Systematic absences caused by different Bravais lattices.

Bravais lattice	Allowed reflections	Extinct (forbidden) reflections
P	All	None
I	$h+k+l = 2n$	$h+k+l = 2n+1$
F	$h+k = 2n$ and $k+l = 2n$ and $h+l = 2n^a$	$h+k = 2n+1$ or $k+l = 2n+1$ or $h+l = 2n+1$
A	$k+l = 2n$	$k+l = 2n+1$
B	$h+l = 2n$	$h+l = 2n+1$
C	$h+k = 2n$	$h+k = 2n+1$
R ^b	$-h+k+l = 3n$ (hexagonal basis)	$-h+k+l = 3n+1$ and $3n+2$
R ^c	$h-k+l = 3n$ (hexagonal basis)	$h-k+l = 3n+1$ and $3n+2$

^a Alternative definition: all indices even ($h=2n$ and $k=2n$ and $l=2n$) or all odd ($h=2n+1$ and $k=2n+1$ and $l=2n+1$).

^b Standard setting.

^c Reverse setting.

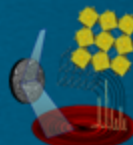


Table 9.8. Reflection conditions for the hexagonal crystal system. There are no space groups with a unique set of reflection conditions.

Reflection conditions				Diffraction symbol	Laue Class				
					6/m		6/mmm		
hkl	h0l	hhl	00l		Point group, space groups				
					6, -6	6/m	622, 6mm	-62m, -6m2	6/mmm
				P $\bar{6}$ ¹⁶⁸	P6/m ¹⁷⁵	P622 ¹⁷⁷	P-62m ¹⁸⁹	P6/mmm ¹⁹¹	
				P-6 ¹⁷⁴		P6mm ¹⁸³	P-6m2 ¹⁸⁷		
		1	P6 ₃	P6 ₃ ¹⁷³	P6 ₃ /m ¹⁷⁶	P6 ₃ 22 ¹⁸²			
		1 ₃ ^b	P6 ₂ $\bar{6}$ ¹⁷¹	P6 ₂ ¹⁷¹		P6 ₂ 22 ¹⁸⁰			
				P6 ₄ ¹⁷²		P6 ₄ 22 ¹⁸¹			
		1 ₆ ^b	P6 ₁ $\bar{6}$ ¹⁶⁹	P6 ₁ ¹⁶⁹		P6 ₁ 22 ¹⁷⁸			
				P6 ₅ ¹⁷⁰		P6 ₅ 22 ¹⁷⁹			
		1	1	P $\bar{6}$ c ^a		P6 ₃ mc ¹⁸⁶	P-62c ¹⁹⁰	P6 ₃ /mmc ¹⁹⁴	
	1		1	P-c $\bar{6}$ ^a		P6 ₃ cm ¹⁸⁵	P-6c2 ¹⁸⁸	P6 ₃ /mcm ¹⁹³	
	1	1	1	P-cc		P6cc ¹⁸⁴		P6/mcc ¹⁹²	