

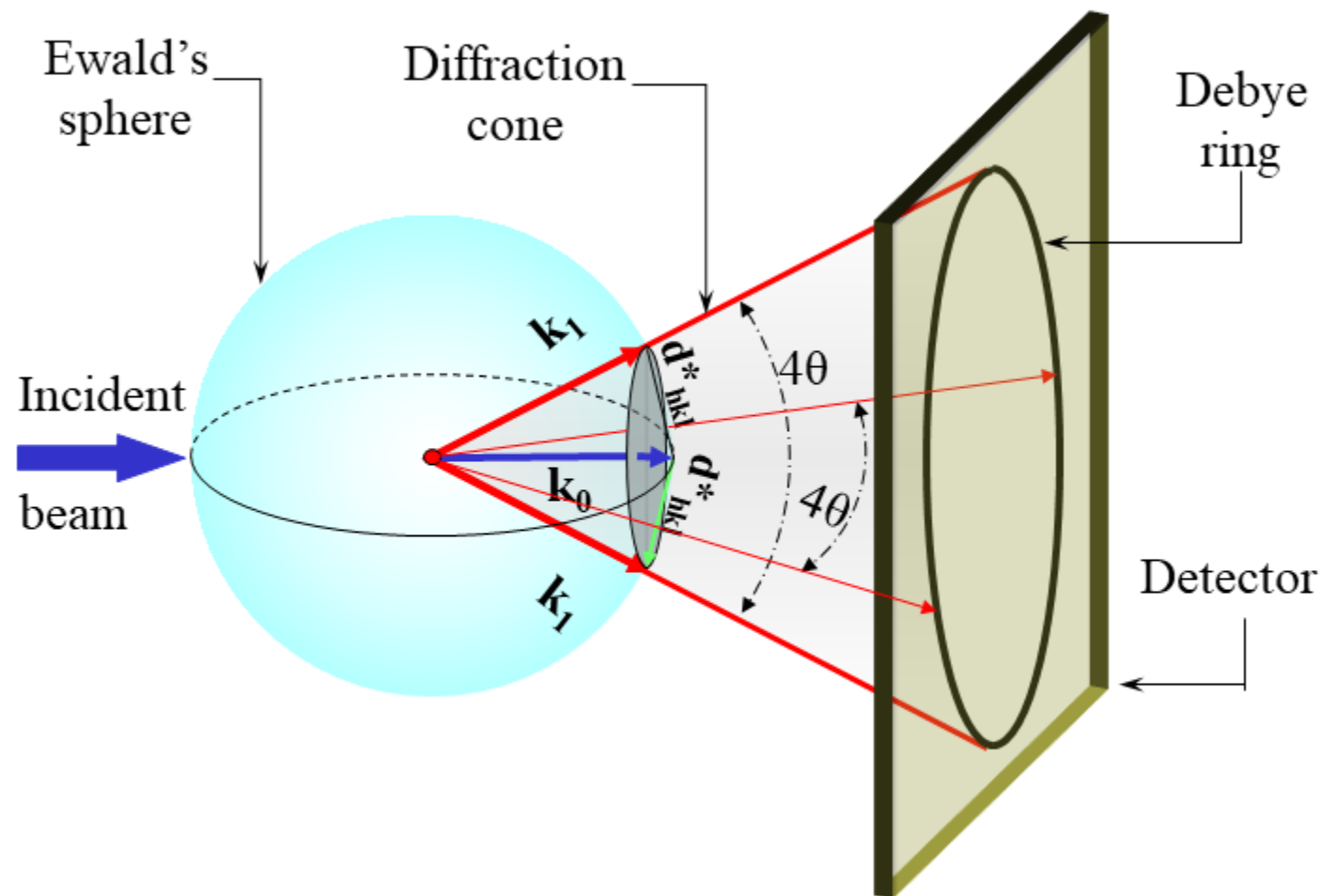
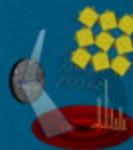


Figure 8.1. The powder diffraction cone originates from the infinite number of completely randomly oriented, identical reciprocal lattice vectors, d_{hkl}^* , which form a circle with their ends placed on the surface of Ewald's sphere. This arrangement produces the powder diffraction cone and the corresponding Debye ring on the flat screen (film or area detector). The detector is perpendicular to both the direction of the incident beam and the cone axis, and the radius of the Debye ring in this geometry is equal to $SDD \cdot \tan 2\theta$, where SDD is the sample-to-detector distance.

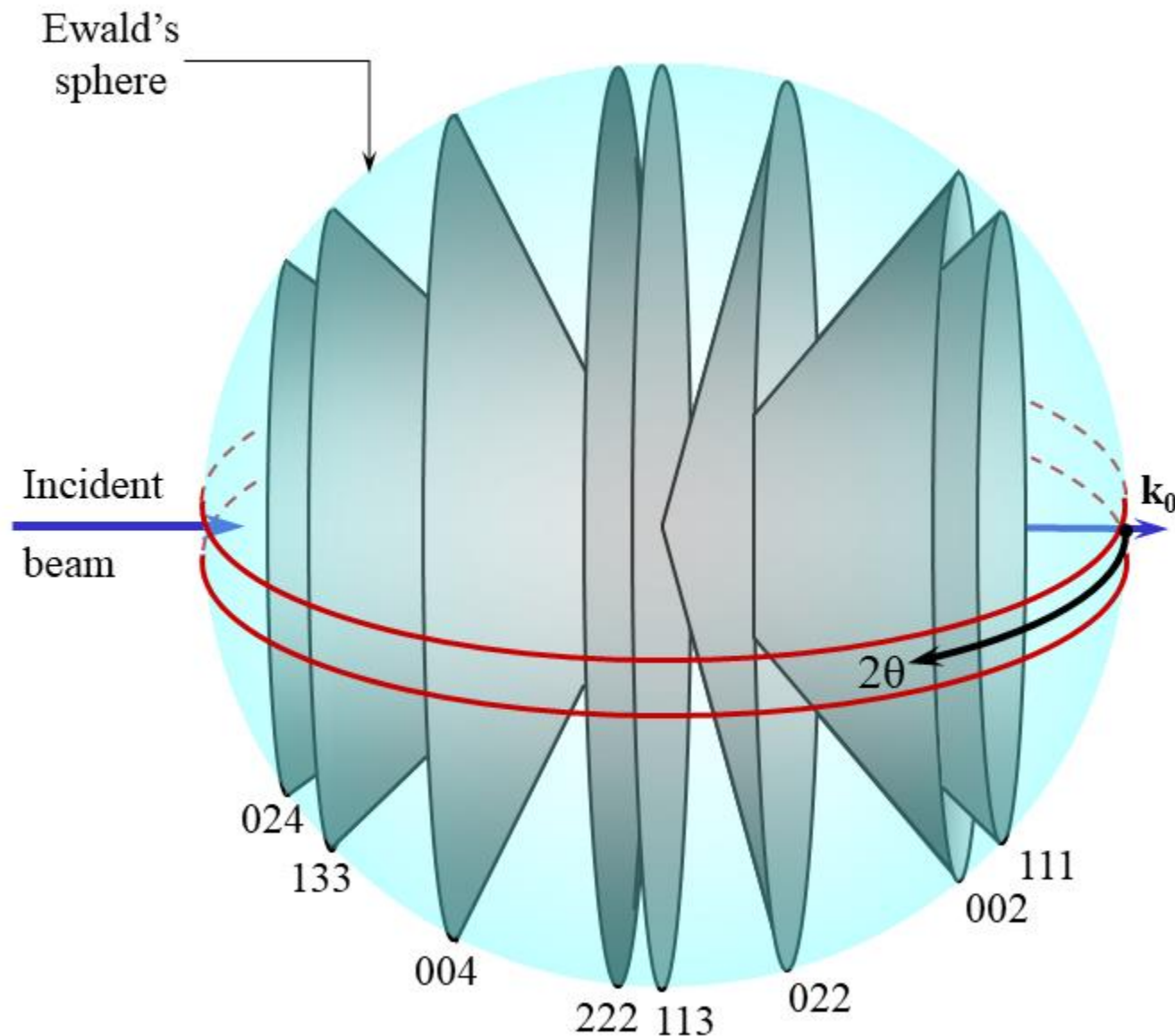


Figure 8.2. The schematic of the powder diffraction cones produced by a polycrystalline copper sample using $\text{Cu K}\alpha_1$ radiation. The differences in the relative intensities of various Bragg peaks (diffraction cones) are not discriminated. Each cone is marked with the corresponding triplet of Miller indices. The *red* cylinder around the equator depicts the portion of the Ewald's sphere scanned during the diffraction experiment using a point or 1D detector.

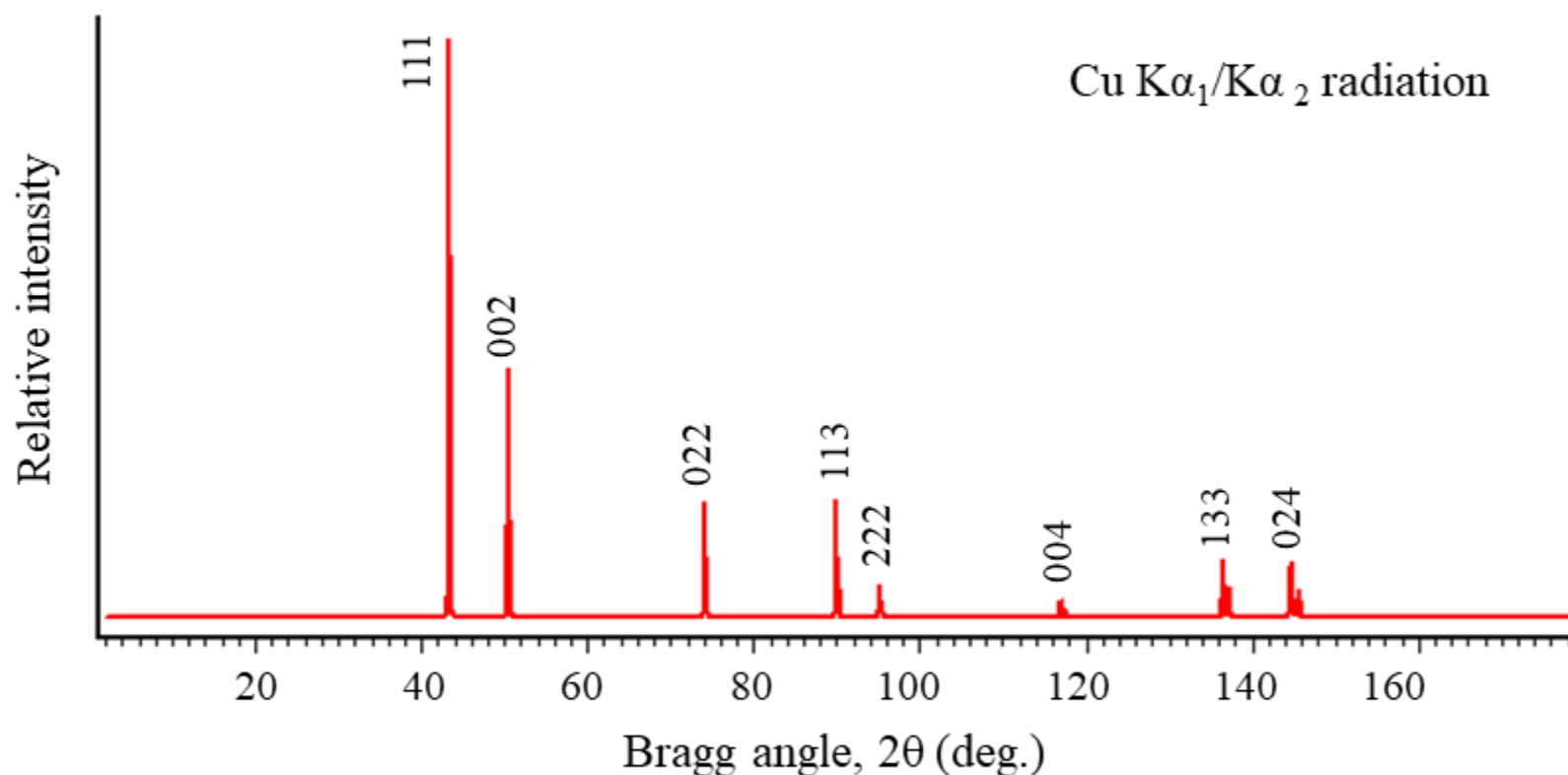
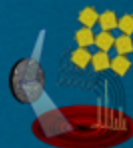


Figure 8.3. The simulated powder diffraction pattern of copper (space group $Fm\bar{3}m$, $a = 3.615 \text{ \AA}$, $\text{Cu}K\alpha_1/K\alpha_2$ radiation, Cu atom in 4(a) position with $x = 0, y = 0, z = 0$).

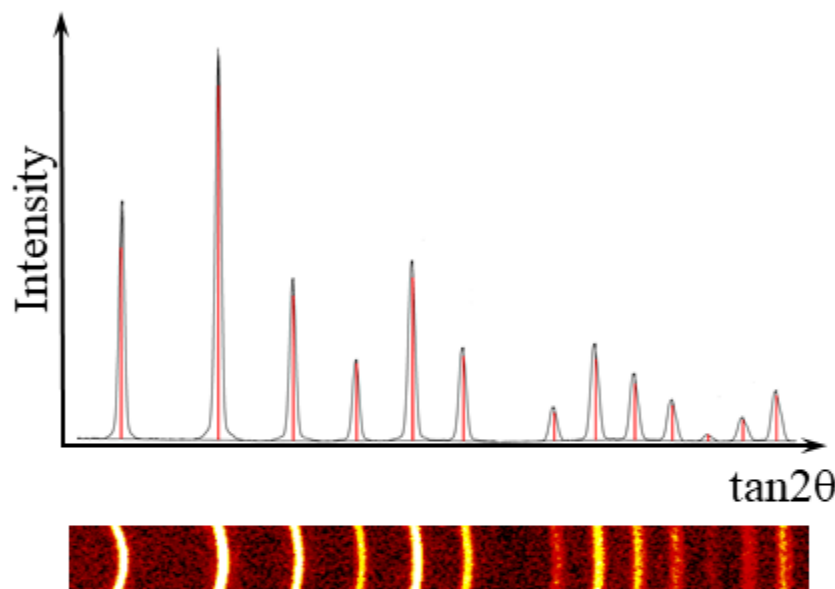
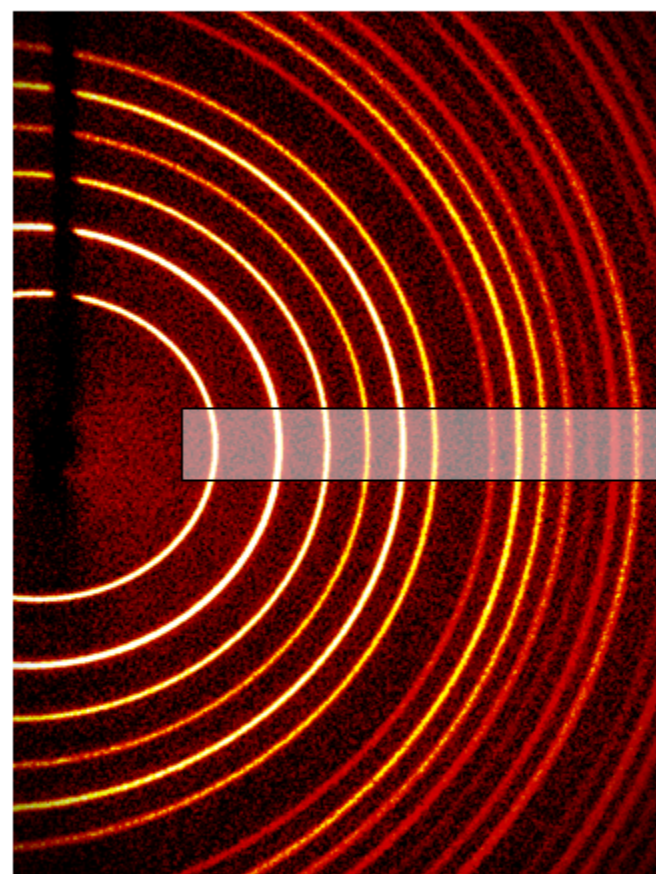
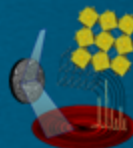


Figure 8.4. *Left* – the X-ray diffraction pattern of a polycrystalline LaB_6 obtained using Mo $K\alpha$ radiation and recorded using a flat CCD area detector (compare with Figure 8.1 and Figure 8.2). Measured intensity is proportional to the degree of darkening. The *dark shadow* extending from the center of the image to the *top* is the projection of the beam stop needed to protect the detector from being damaged by the high intensity incident beam.

The *light shaded rectangular box* delineates the area in which the scattered intensity was integrated from the center of the image toward its right edge. *Right* – the resultant intensity as a function of $\tan 2\theta$ shown together with the area over which the integration has been carried out.

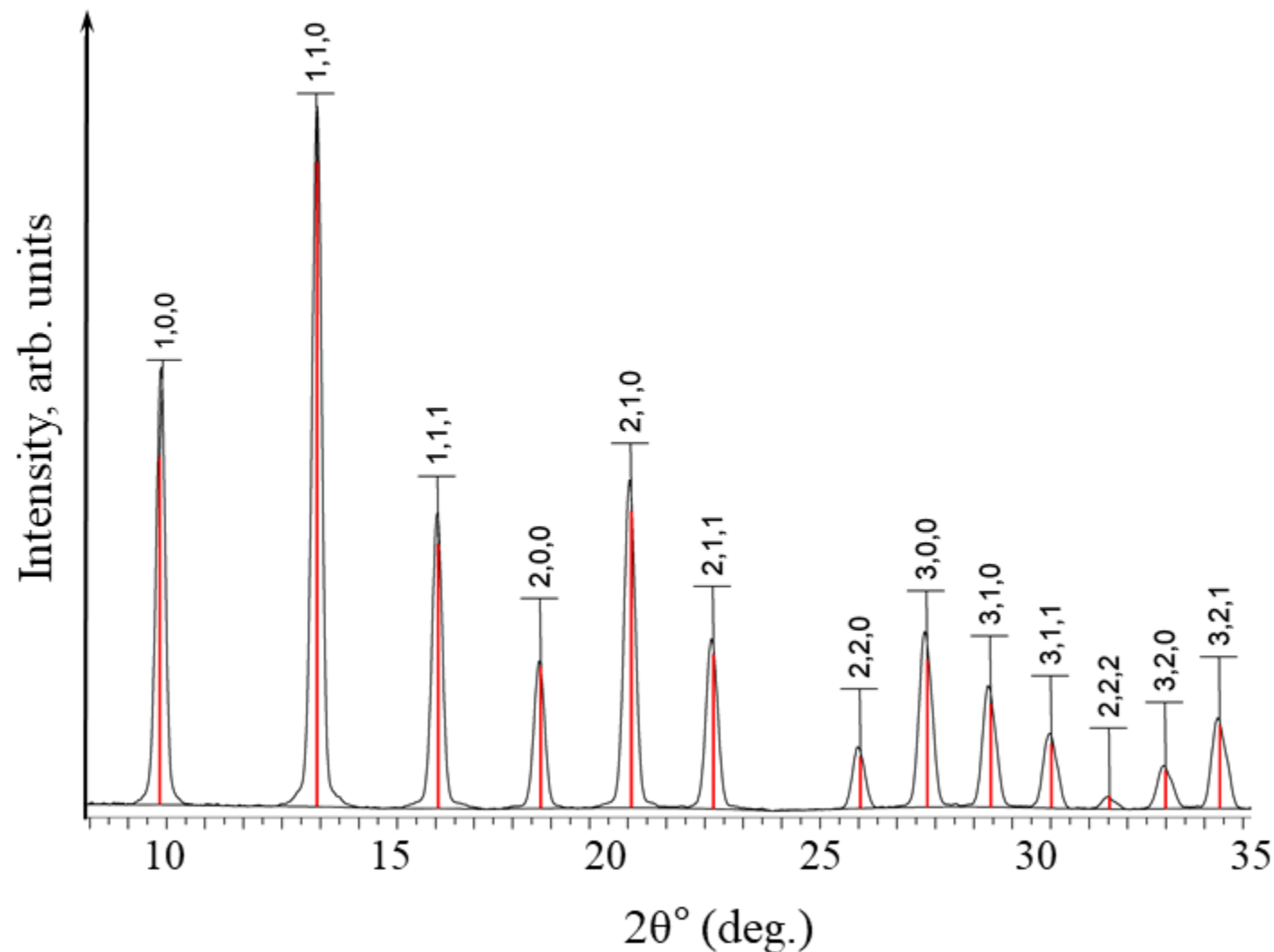
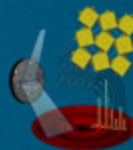


Figure 8.5. The powder diffraction pattern of the polycrystalline LaB_6 as intensity versus 2θ obtained by the integration of the rectangular area from the two-dimensional diffraction pattern shown in Figure 8.4.

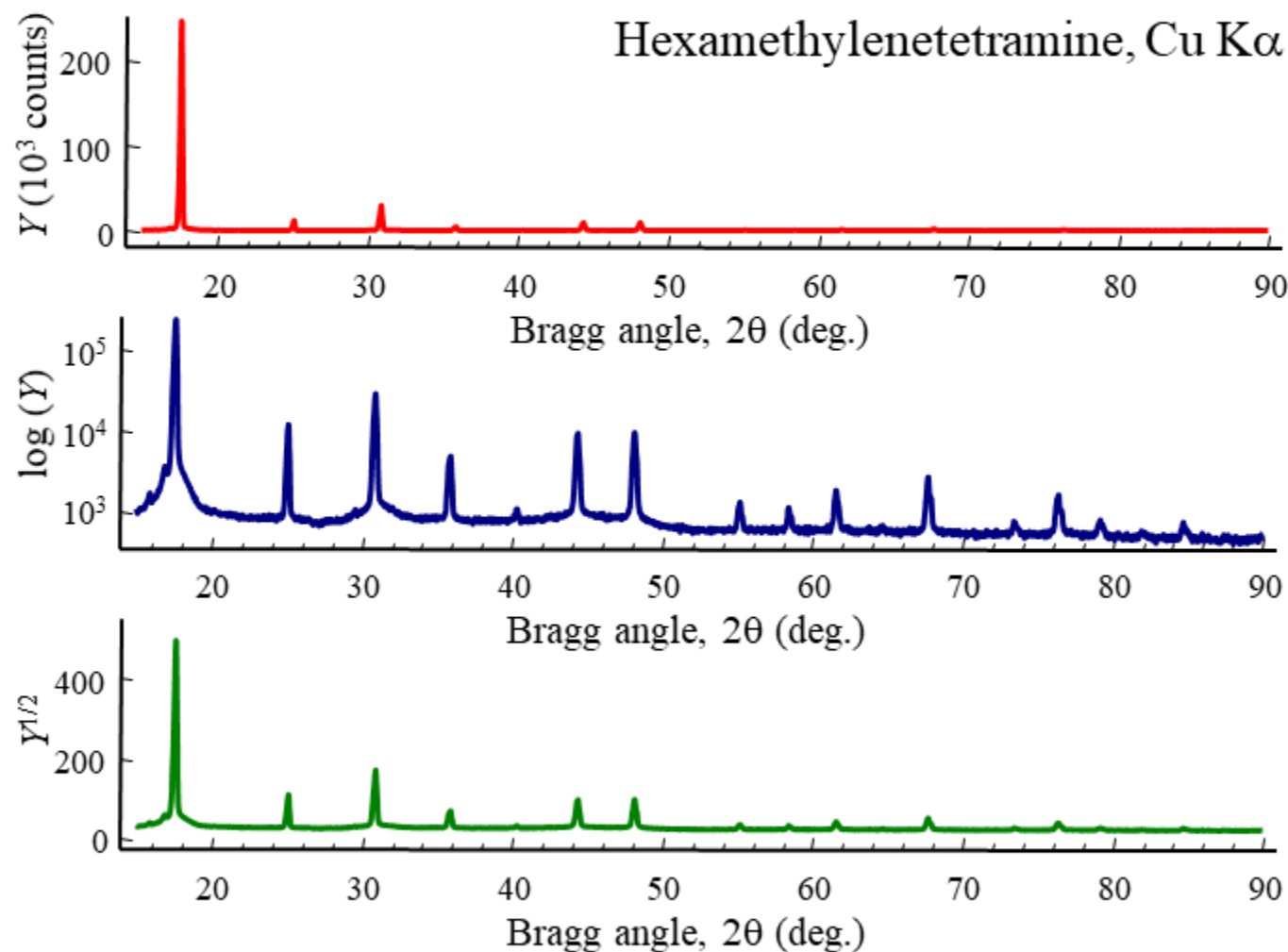
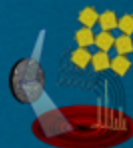


Figure 8.6. The powder diffraction pattern of hexamethylenetetramine collected using Cu $K\alpha$ radiation and plotted as the measured intensity in counts (*top*), common logarithm (*middle*), and square root (*bottom*) of the total number of registered photon counts versus 2θ .

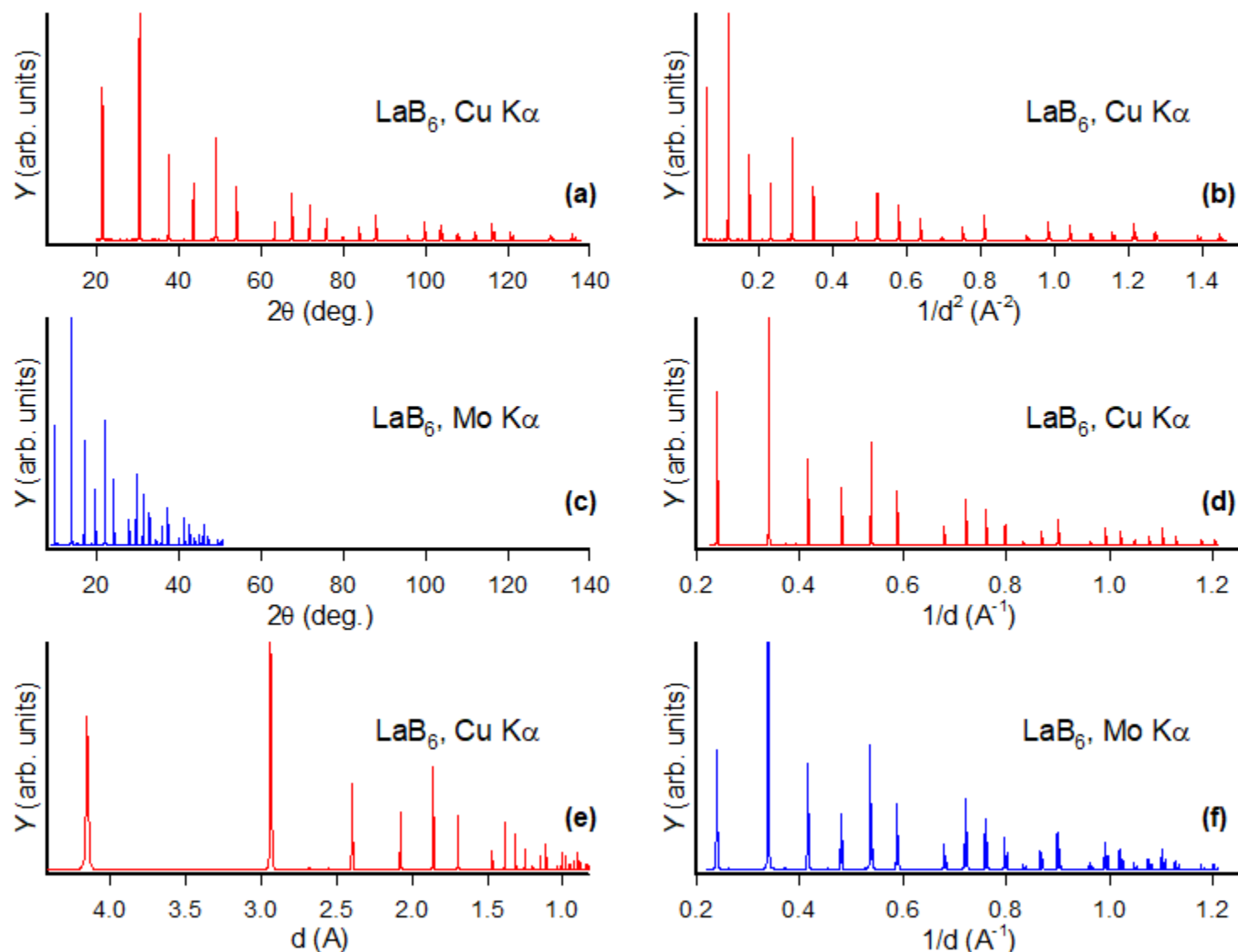
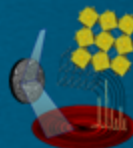


Figure 8.7. Two powder diffraction patterns of LaB_6 collected using different wavelengths with the scattered intensity plotted versus different independent variables. Each plot contains the same number of Bragg peaks, which can be observed below $2\theta \cong 140^\circ$ when using $\text{Cu K}\alpha$ radiation.

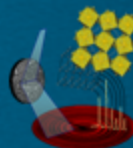


Table 8.2. Powder diffraction pattern as a function of various crystal structure, specimen and instrumental parameters.^a

Pattern component	Crystal structure	Specimen property	Instrumental parameter
Peak position	Unit cell parameters: (a,b,c,α,β,γ)	<i>Absorption</i> <i>Porosity</i>	Radiation (wavelength) <i>Instrument/sample alignment</i> <i>Axial divergence of the beam</i>
Peak intensity	Atomic parameters (x, y, z, B, etc.)	<i>Preferred orientation</i> <i>Absorption</i> <i>Porosity</i>	<i>Geometry and configuration</i> Radiation (Lorentz, polarization)
Peak shape	<i>Crystallinity</i> <i>Disorder</i> <i>Defects</i>	<i>Grain size</i> <i>Strain</i> <i>Stress</i>	Radiation (spectral purity) Geometry Beam conditioning

^a Key parameters are shown in **bold**. Parameters with a significant influence are shown in *italic*.

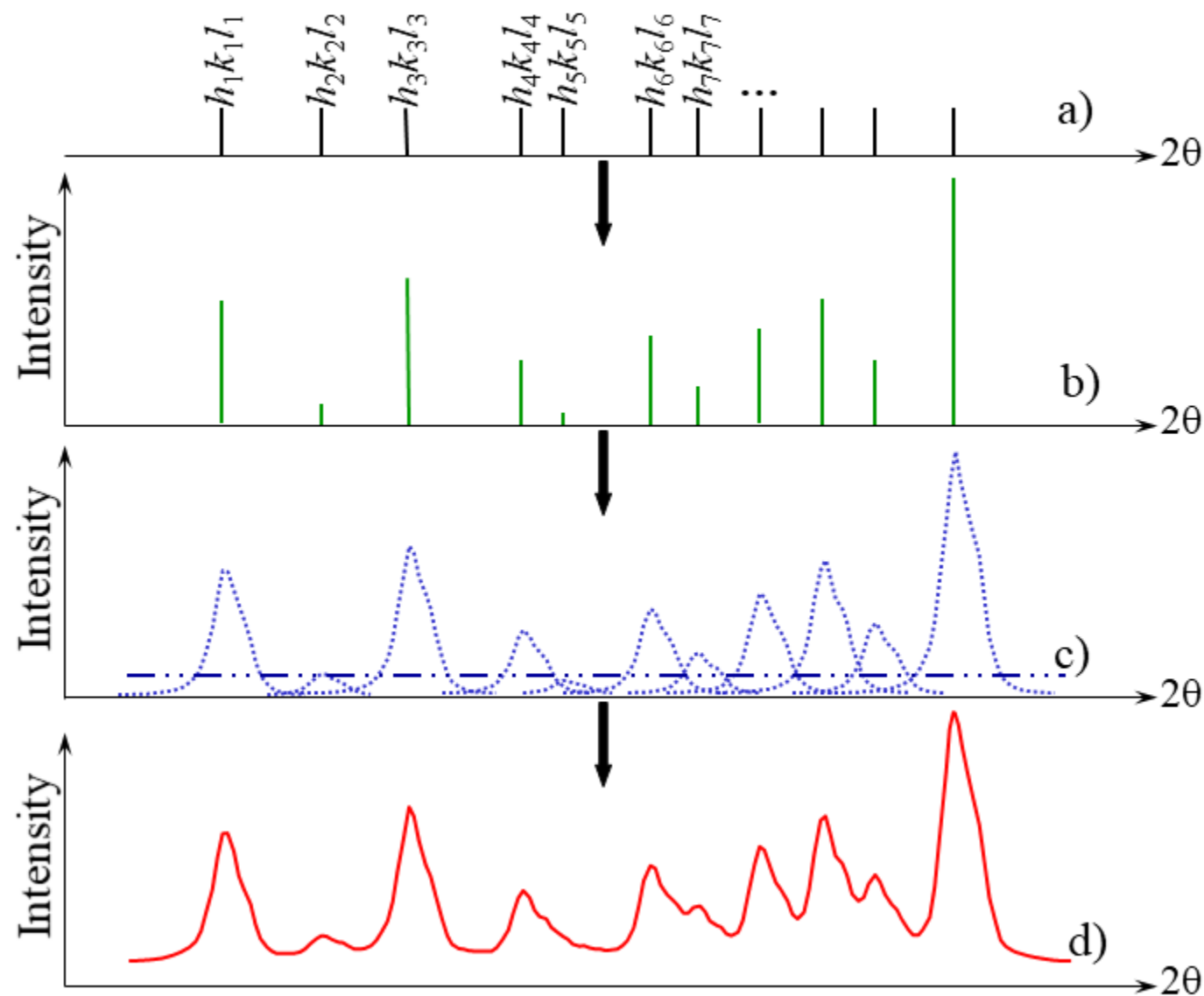
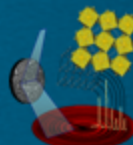


Figure 8.8. The appearance of the powder diffraction pattern: (a) only Bragg peak positions (e.g., see Eq. 8.1) are represented by the *vertical bars* of equal length; (b) in addition to peak positions, their intensities are indicated by using the bars with variable lengths (the higher the intensity, the *longer the bar*); (c) peak shapes have been introduced by substituting individual intensities with appropriate peak-shape functions, and a constant background has been indicated by the *dash-double dotted line*; (d) the resultant powder diffraction pattern is the sum of all components shown separately in (c), i.e., discrete but partially overlapped peaks and continuous background.

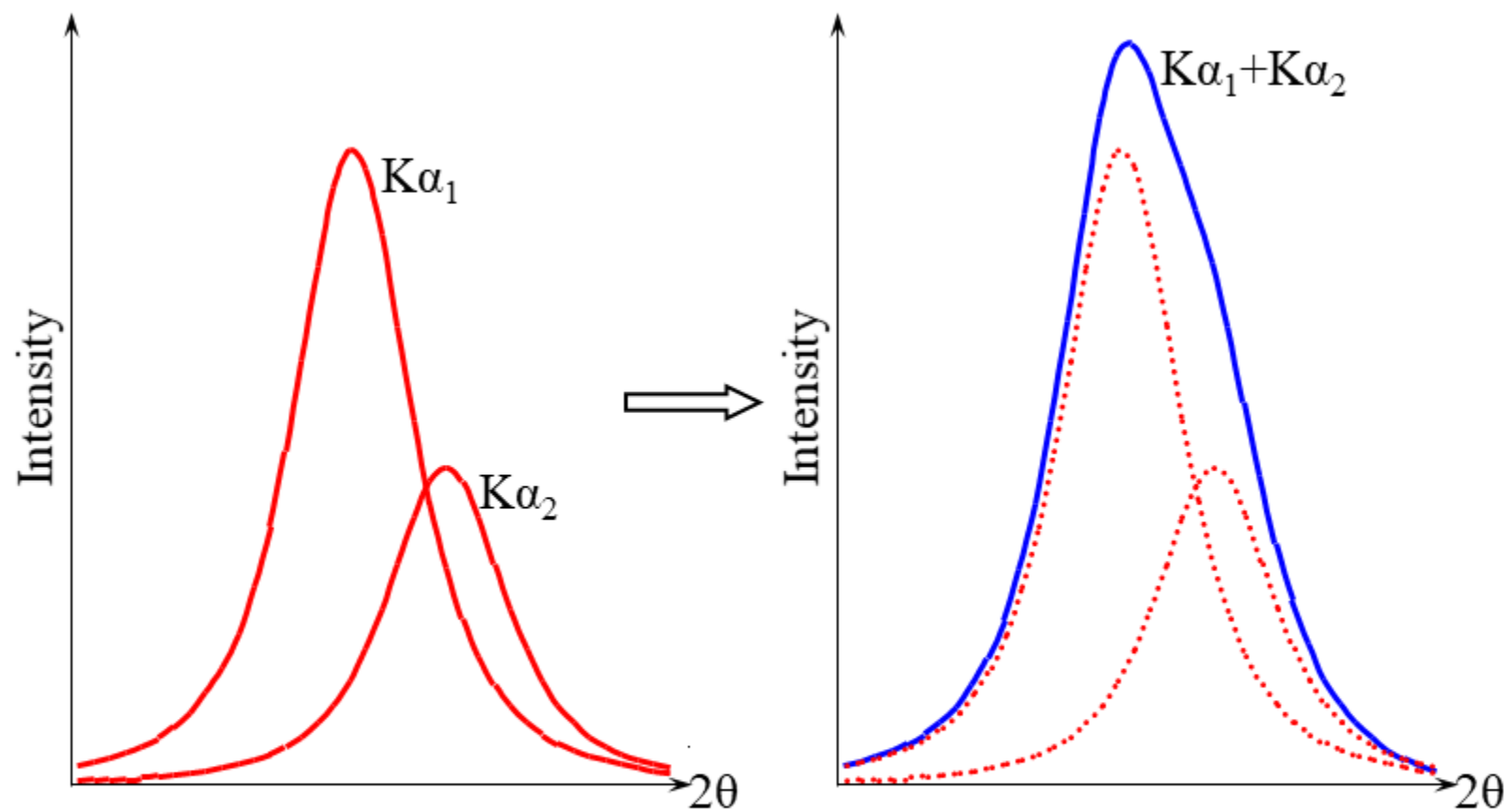
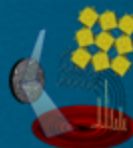
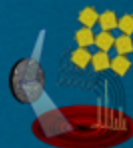


Figure 8.9. The two individual – functions corresponding to monochromatic $K\alpha_1$ and $K\alpha_2$ wavelengths (*left*) and the combined peak-shape function for a $K\alpha_1/K\alpha_2$ doublet as the sum of two peaks (*right*). Since both $K\alpha_1$ and $K\alpha_2$ peaks correspond to the same $\mathbf{d}^*_{hkl}$, their positions, θ_1 and θ_2 , are related as $\sin\theta_1/\lambda K\alpha_1 = \sin\theta_2/\lambda K\alpha_2$ (see Eq. 7.9), while their areas (intensities) are related as approximately 2 to 1.



Peak Positions as a Function of Unit Cell Dimensions:

Cubic: $\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$ Eq. 8.2

Tetragonal: $\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$ Eq. 8.3

Hexagonal: $\frac{1}{d^2} = \frac{4}{3} \frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2}$ Eq. 8.4

Orthorhombic: $\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$ Eq. 8.5

Monoclinic: $\frac{1}{d^2} = \frac{h^2}{a^2 \sin^2 \beta} + \frac{k^2}{b^2} + \frac{l^2}{c^2 \sin^2 \beta} + \frac{2hl \cos \beta}{ac \sin^2 \beta}$ Eq. 8.6

Triclinic: $\frac{1}{d^2} = \left[\frac{h^2}{a^2 \sin^2 \alpha} + \frac{2kl}{bc} (\cos \beta \cos \gamma - \cos \alpha) + \frac{k^2}{b^2 \sin^2 \beta} + \frac{2hl}{ac} (\cos \alpha \cos \gamma - \cos \beta) + \frac{l^2}{c^2 \sin^2 \gamma} + \frac{2hk}{ab} (\cos \alpha \cos \beta - \cos \gamma) \right] /$ Eq. 8.7

$$(1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma)$$

$$2\theta_{hkl} = 2 \arcsin \left(\frac{\lambda}{2d_{hkl}} \right)$$

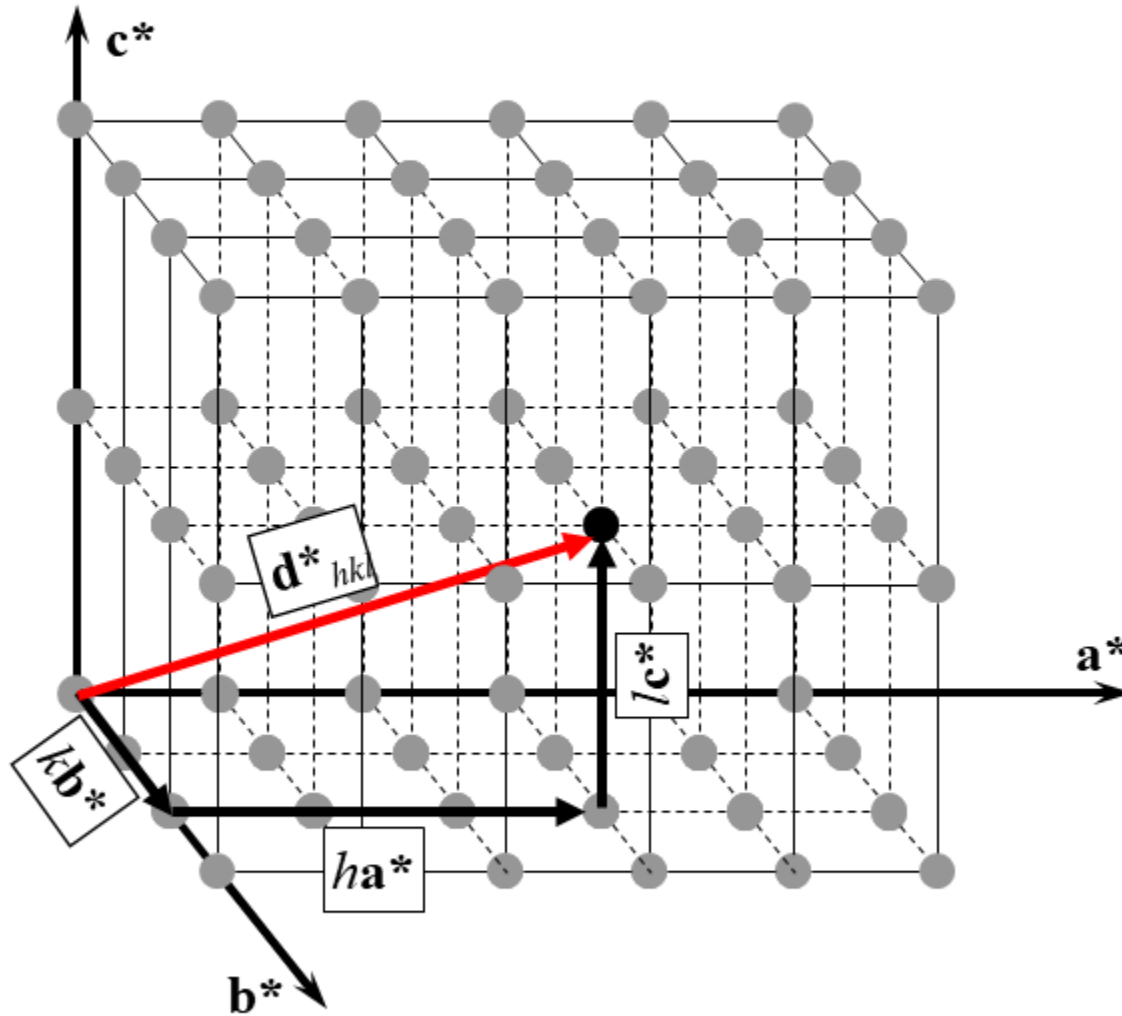
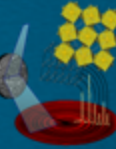
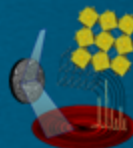


Figure 8.10. The illustration of a reciprocal lattice vector, d^*_{hkl} (red), as a vectorial sum of three basis unit vectors, a^* , b^* and c^* multiplied by h , k and l , respectively.

$$\mathbf{d}^*_{hkl} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* \quad \text{Eq. 8.8}$$

$$\begin{aligned} d^{*2} = & h^2 a^{*2} + k^2 b^{*2} + l^2 c^{*2} \\ & + 2hka^*b^* \cos \gamma^* \\ & + 2hla^*c^* \cos \beta^* \\ & + 2klb^*c^* \cos \alpha^* \end{aligned} \quad \text{Eq. 8.10}$$



Other Factors Affecting Peak Positions: $2\theta_{obs} = 2\theta_{calc} + \Delta 2\theta$ **Eq. 8.12**

$$\Delta 2\theta = \frac{p_1}{\tan 2\theta} + \frac{p_2}{\sin 2\theta} + \frac{p_3}{\tan \theta} + p_4 \sin 2\theta + p_5 \cos \theta + p_6$$
 Eq. 8.13

Axial Divergence: $p_1 = -\frac{h^2 K_1}{3R^2}; \quad p_2 = -\frac{h^2 K_2}{3R^2}$ **Eq. 8.14**

In-plane divergence: $p_3 = -\frac{\alpha^2}{K_3}$ **Eq. 8.15**

Transparency shift: $p_4 = \frac{1}{2\mu_{eff}R}$ **Eq. 8.16**

Sample displacement: $p_5 = -\frac{2s}{R}$ **Eq. 8.17**

Zero shift (deg): p_6

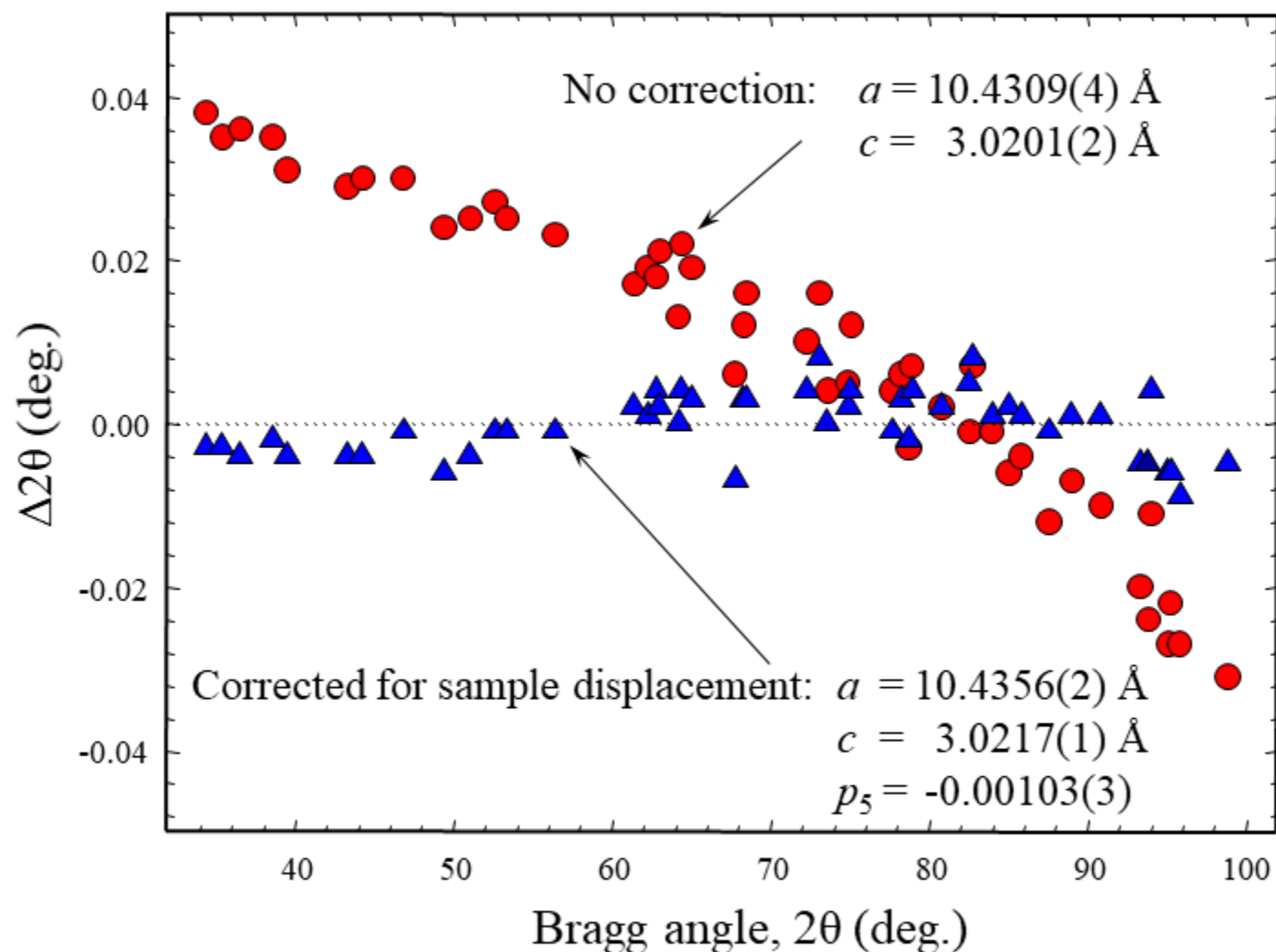
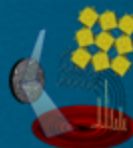
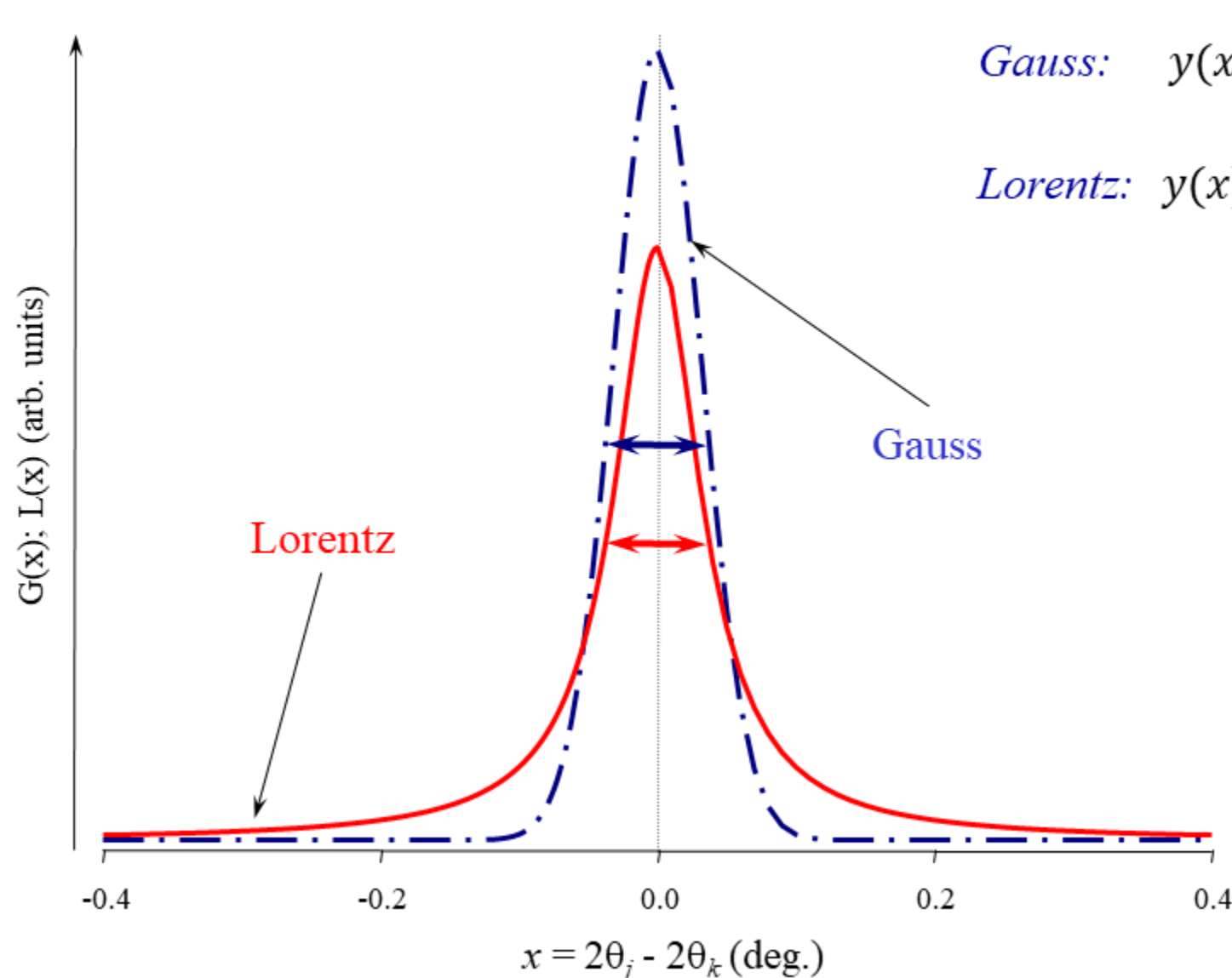
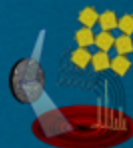


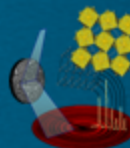
Figure 8.11. The differences between the observed and calculated 2θ values plotted as a function of 2θ without (*red circles*) and with (*blue triangles*) specimen displacement correction. The corresponding values of the unit cell parameters and the specimen displacement parameter are indicated on the plot. The material belongs to the tetragonal crystal system.



$$\text{Gauss: } y(x) = G(x) = \frac{C_G^{1/2}}{\sqrt{\pi}H} \exp(-C_G x^2) \quad \text{Eq. 8.22}$$

$$\text{Lorentz: } y(x) = L(x) = \frac{C_L^{1/2}}{\pi H'} (1 + C_L x^2)^{-1} \quad \text{Eq. 8.23}$$

Figure 8.12. The illustration of Gauss (*dash-dotted line*) and Lorentz (*solid line*) peak-shape functions. Both functions have been normalized to result in identical definite integrals ($\int_{-\infty}^{\infty} G(x)dx = \int_{-\infty}^{\infty} L(x)dx$) and full widths at half maximum (FWHM). The corresponding FWHM's are shown as *thick horizontal arrows*.



Pseudo-Voigt (PV) Peak Shape Function commonly used to fit X-ray data:

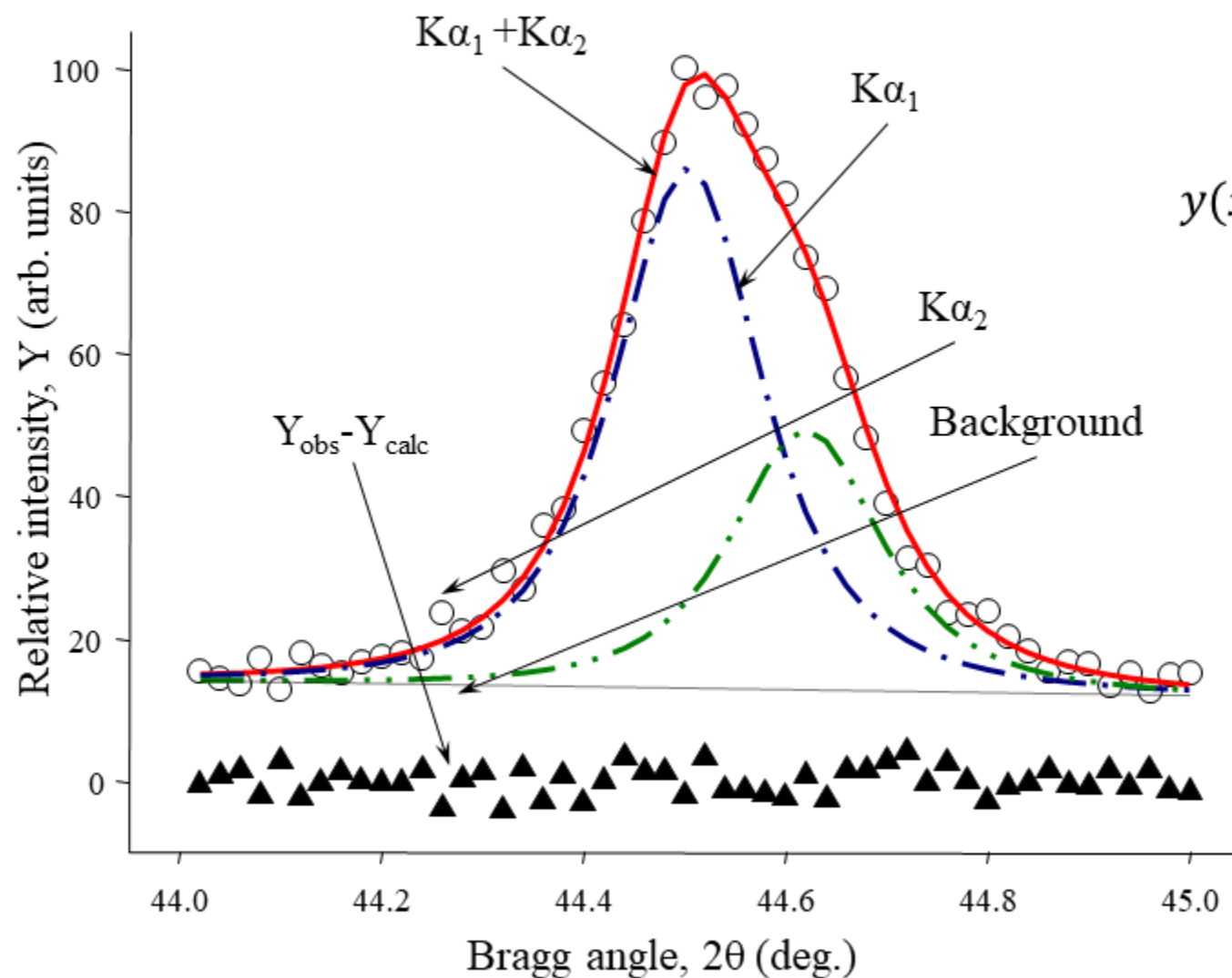
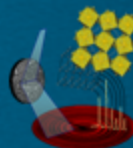
$$y(x) = \eta \frac{C_G^{1/2}}{\sqrt{\pi}H} \exp(-C_G x^2) + (1 - \eta) \frac{C_L^{1/2}}{\pi H'} (1 + C_L x^2)^{-1} \quad \text{Eq. 8.24}$$

where:

- H and H' are the full widths at half maximum (often abbreviated as FWHM).
- $x = (2\theta_i - 2\theta_k)/H_k$, is the Bragg angle of the i^{th} point with its origin in the position of the k^{th} peak divided by the peak's FWHM.
- $2\theta_i$ is the Bragg angle of the i^{th} point of the powder diffraction pattern;
- $2\theta_k$ is the calculated (or ideal) Bragg angle of the k^{th} Bragg reflection.
- $C_G = 4 \ln 2$ and $C_G^{1/2}/\sqrt{\pi}H$ are the normalization factors for the Gauss function such that $\int_{-\infty}^{\infty} G(x)dx = 1$.
- $C_L = 4$ and $C_L^{1/2}/\pi H'$ are the normalization factors for the Lorentz function such that $\int_{-\infty}^{\infty} L(x)dx = 1$.
- $H = (U \tan^2 \theta + V \tan \theta + W)^{1/2}$, also known as Caglioti formula, is the full width at half maximum as a function of θ .
- $H' = X/\cos \theta + Y \tan \theta$ is the full width at half maximum as a function of θ for the Lorentz function.
- $\eta = \eta_0 + \eta_1 2\theta + \eta_2 2\theta^2$, where $0 \leq \eta \leq 1$, is the pseudo-Voigt function mixing parameter of the Gauss and Lorentz functions.

Additionally for Pearson-VII function (see next slide):

- Γ is the gamma function.
- $\beta = \beta_0 + \beta_1/2\theta + \beta_2/(2\theta)^2$, is the exponent as a function of Bragg angle.
- $C_P = 4(2^{1/\beta} - 1)$, and $[\Gamma(\beta)/\Gamma(\beta - 1/2)] C_P^{1/2}/\sqrt{\pi}H$ is the normalization factor such that $\int_{-\infty}^{\infty} PVII(x)dx = 1$.



Pearson-VII function (PVI):

$$y(x) = \frac{\Gamma(\beta)}{\Gamma(\beta - 1/2)} \frac{C_P^{1/2}}{\sqrt{\pi}H} (1 + C_P x^2)^{-\beta} \quad \text{Eq. 8.25}$$

Figure 8.13. The example of using Pearson-VII function (PVI) to fit experimental data (*open circles*) representing a single Bragg peak containing $K\alpha_1$ and $K\alpha_2$ components.

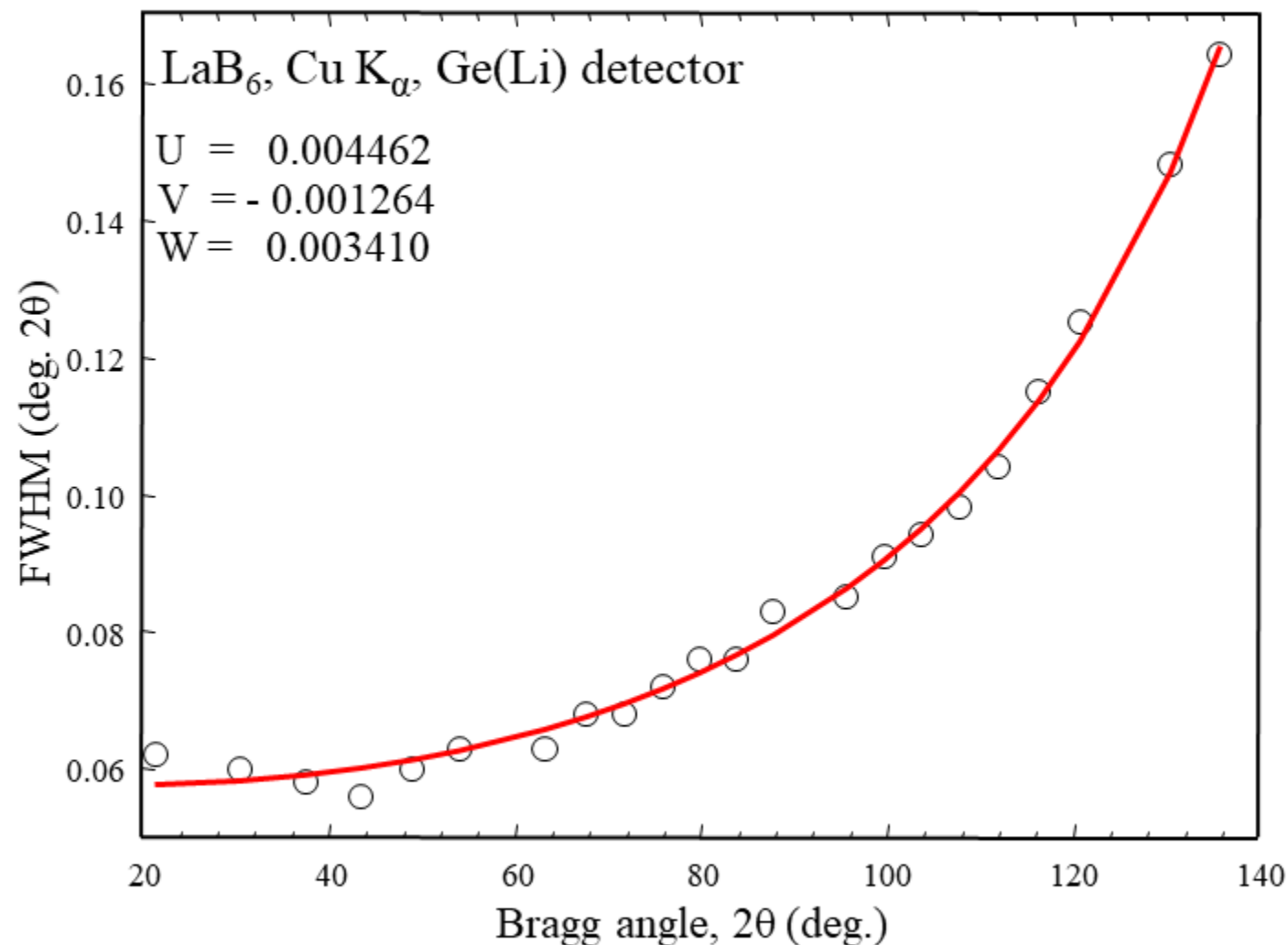
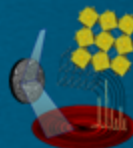
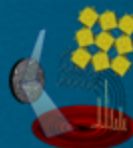


Figure 8.14. Experimentally observed full width at half maximum of LaB₆ (*open circles*) as a function of 2θ . The solid line represents a least squares fit and is calculated using Eq. 8.26, with $U = 0.004462$, $V = -0.001264$, and $W = 0.003410$.

$$H = \sqrt{U \tan^2 \theta + V \tan \theta + W} \quad \text{Eq. 8.26}$$



Peak-shape function (PSF) is a convolution of three different functions:

Ω – instrumental broadening,
 Λ – wavelength dispersion,
 Ψ – specimen function.

$$PSF(\theta) = \Omega(\theta) \otimes \Lambda(\theta) \otimes \Psi(\theta) + b(\theta) \quad \text{Eq. 8.18}$$

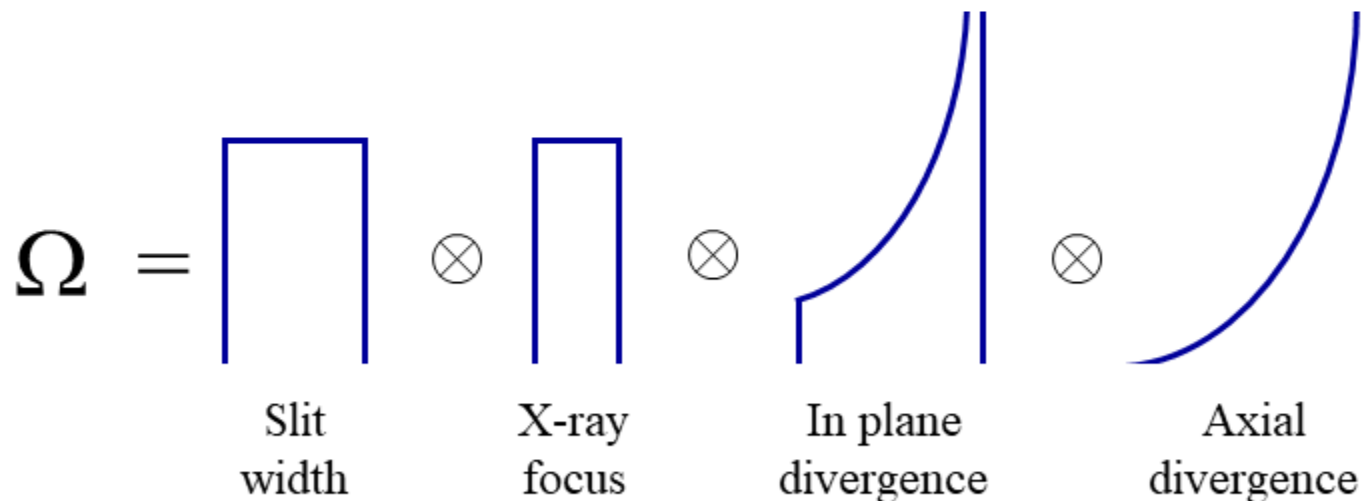


Figure 8.15. Graphical representation of typical fundamental functions defining convoluted instrumental profile.

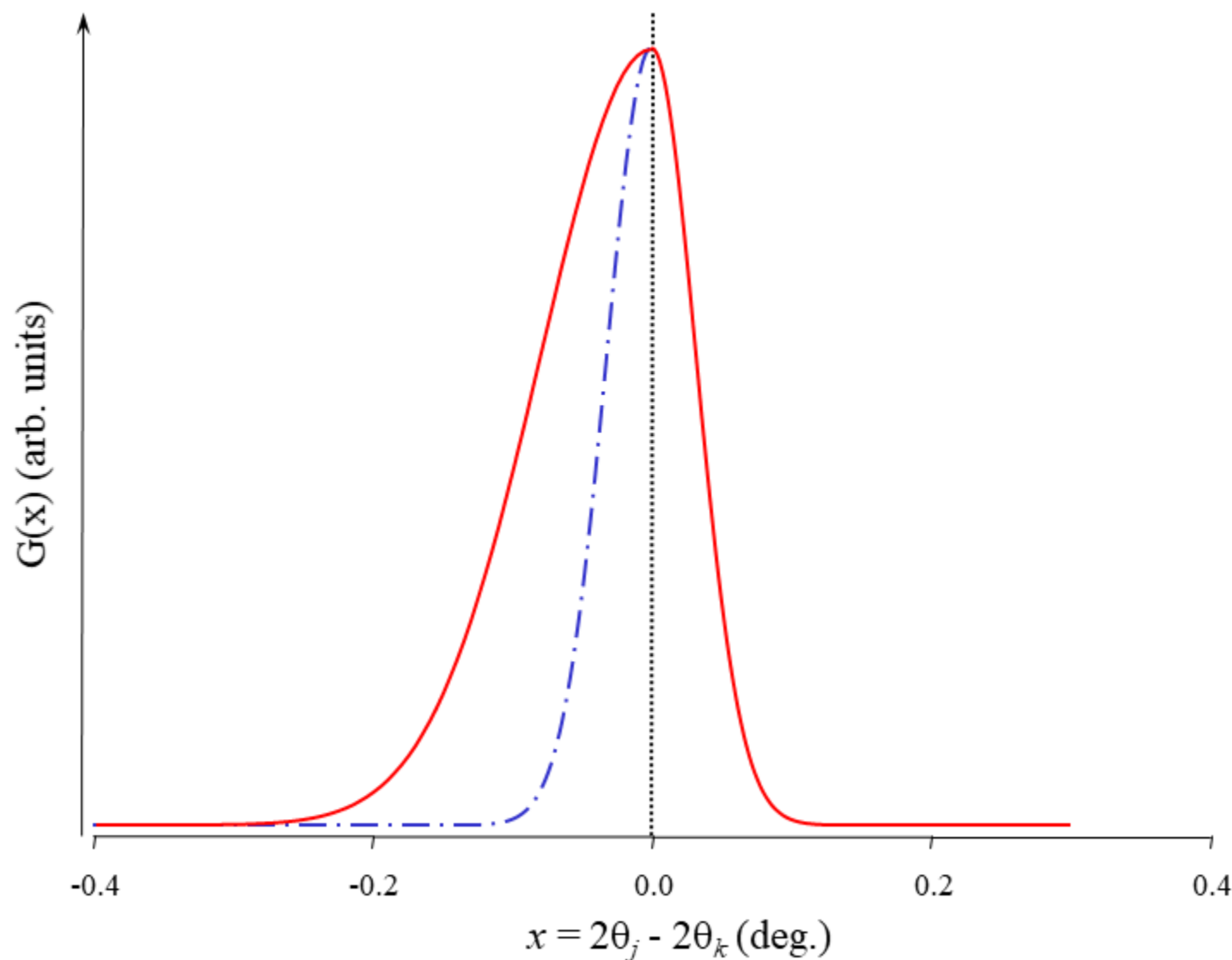
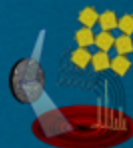


Figure 8.16. The schematic illustrating the asymmetric Bragg peak (*solidline*) when compared with the symmetric peak composed of the dash-dotted line (*left slope*) and the solid line (*right slope*). Both peaks are modeled by the pure Gauss function (Eq. 8.22) using two different FWHM's on different sides of the peak maximum in the asymmetric case.

Asymmetry function for PV:

$$A(x_i) = 1 - \alpha \frac{z_i \times |z_i|}{\tan \theta} \quad \text{Eq. 8.37}$$

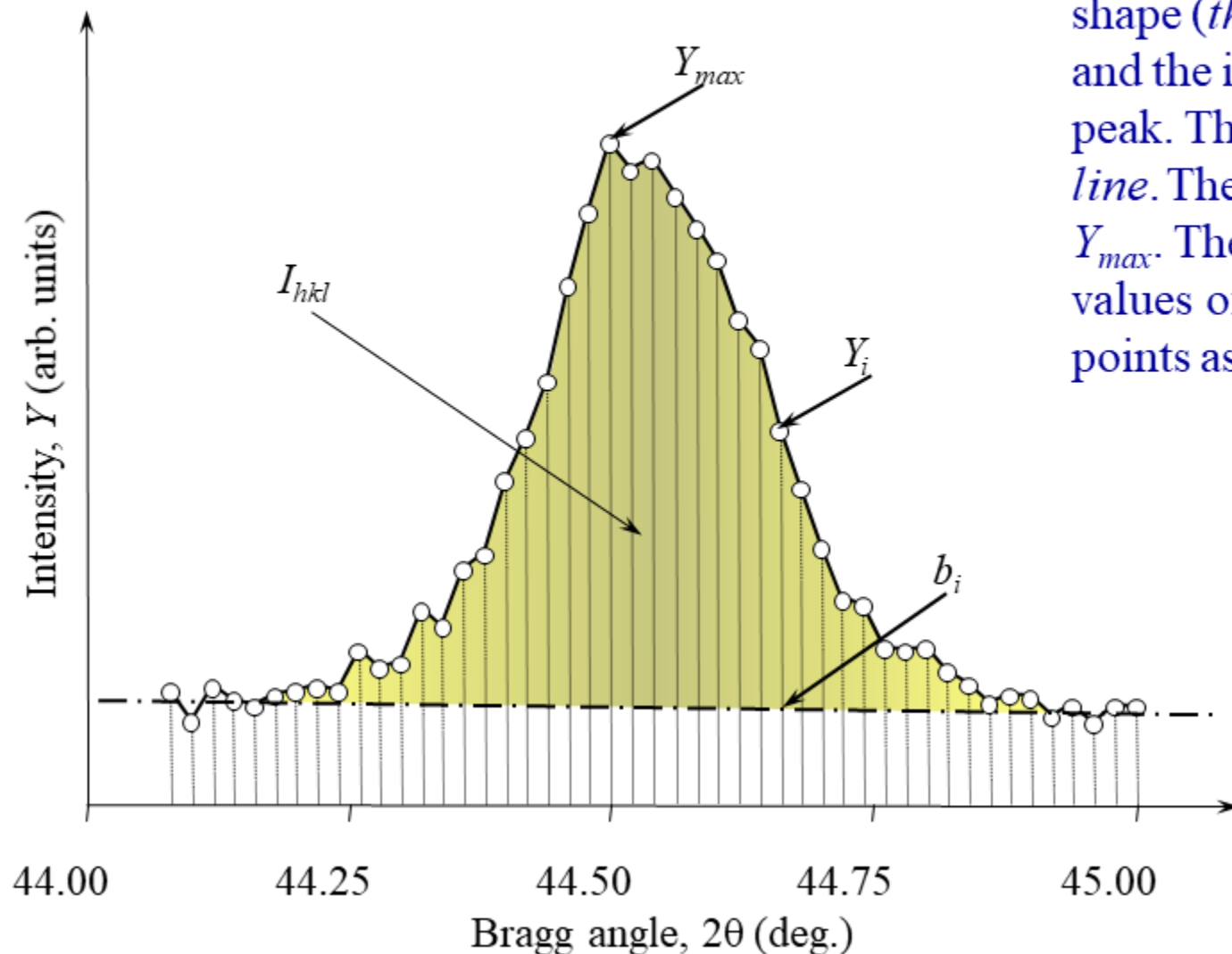
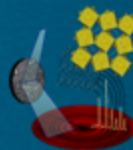
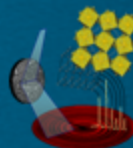


Figure 8.17. The relationship between the measured shape (*the open circles connected with the solid lines*) and the integrated intensity (*shaded area*) of the Bragg peak. The background is shown using *the dash-dotted line*. The maximum measured intensity is indicated as Y_{max} . The measured intensities and the corresponding values of the background are indicated for one of the points as Y_i and b_i , respectively.

$$I_{hkl} = \sum_{i=1}^j (Y_i^{obs} - b_i) \quad \text{Eq. 8.40}$$



Calculated Integrated Intensity in Powder Diffraction:

$$I_{hkl} = K \times p_{hkl} \times L_{\theta} \times P_{\theta} \times A_{\theta} \times T_{hkl} \times E_{hkl} \times |F_{hkl}|^2 \quad \text{Eq. 8.41}$$

where:

- **K is the scale factor**, which normalizes experimentally observed integrated intensities to calculated.
- **p_{hkl} is the multiplicity factor** that accounts for the presence of multiple symmetrically equivalent reflections.
- **L_{θ} is Lorentz factor** defined by the geometry of diffraction.
- **P_{θ} is the polarization factor**, which accounts for a partial polarization of the scattered electromagnetic wave.
- **A_{θ} is the absorption correction** for absorption of both the incident and diffracted beams and nonzero porosity.
- **T_{hkl} is the preferred orientation correction** for non-randomness in the distribution of grain orientations.
- **E_{hkl} is the extinction multiplier** accounting for deviations from the kinematical diffraction model.
- **F_{hkl} is the structure factor** (or the structure amplitude) defined by the crystal structure of the material.

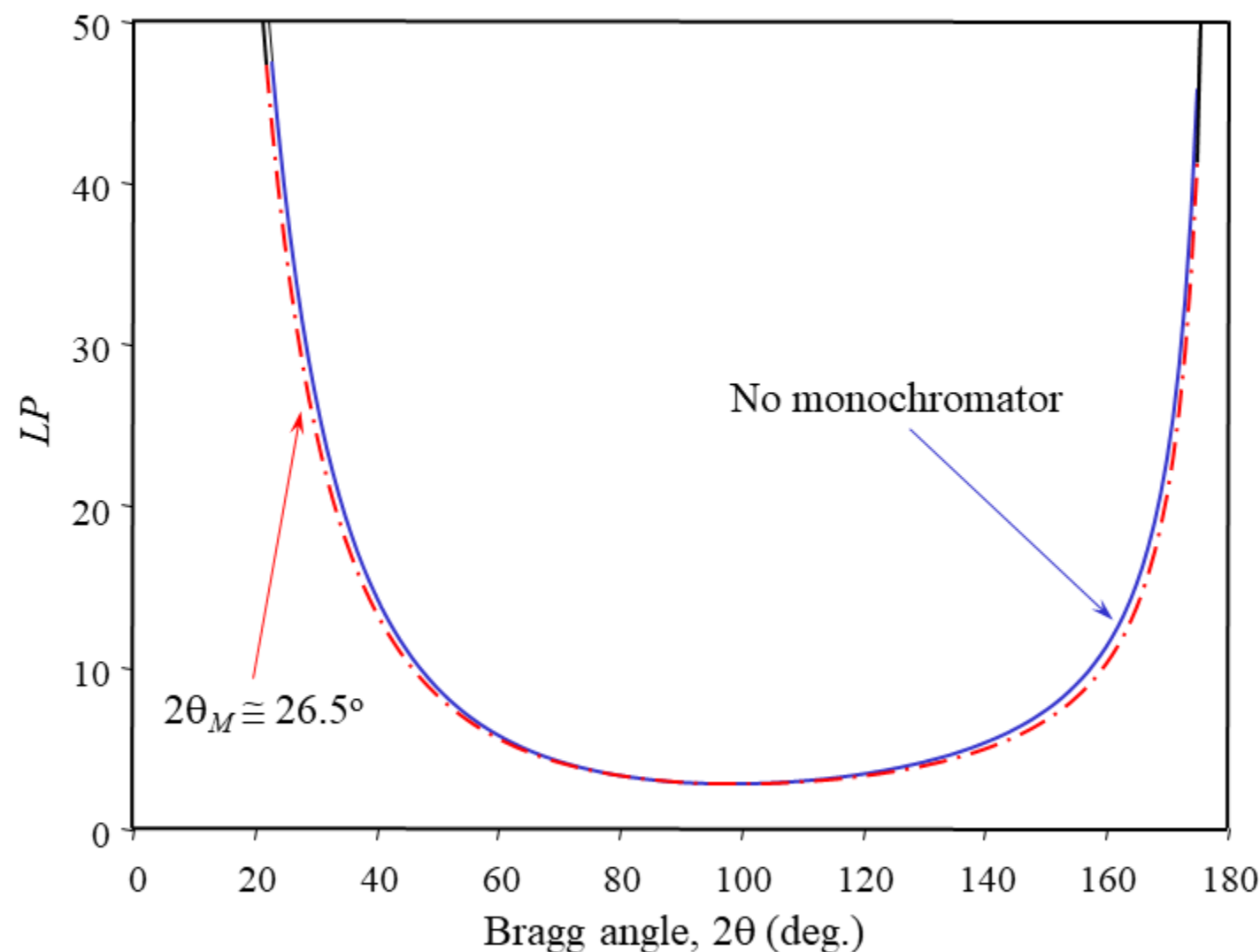
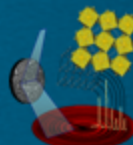
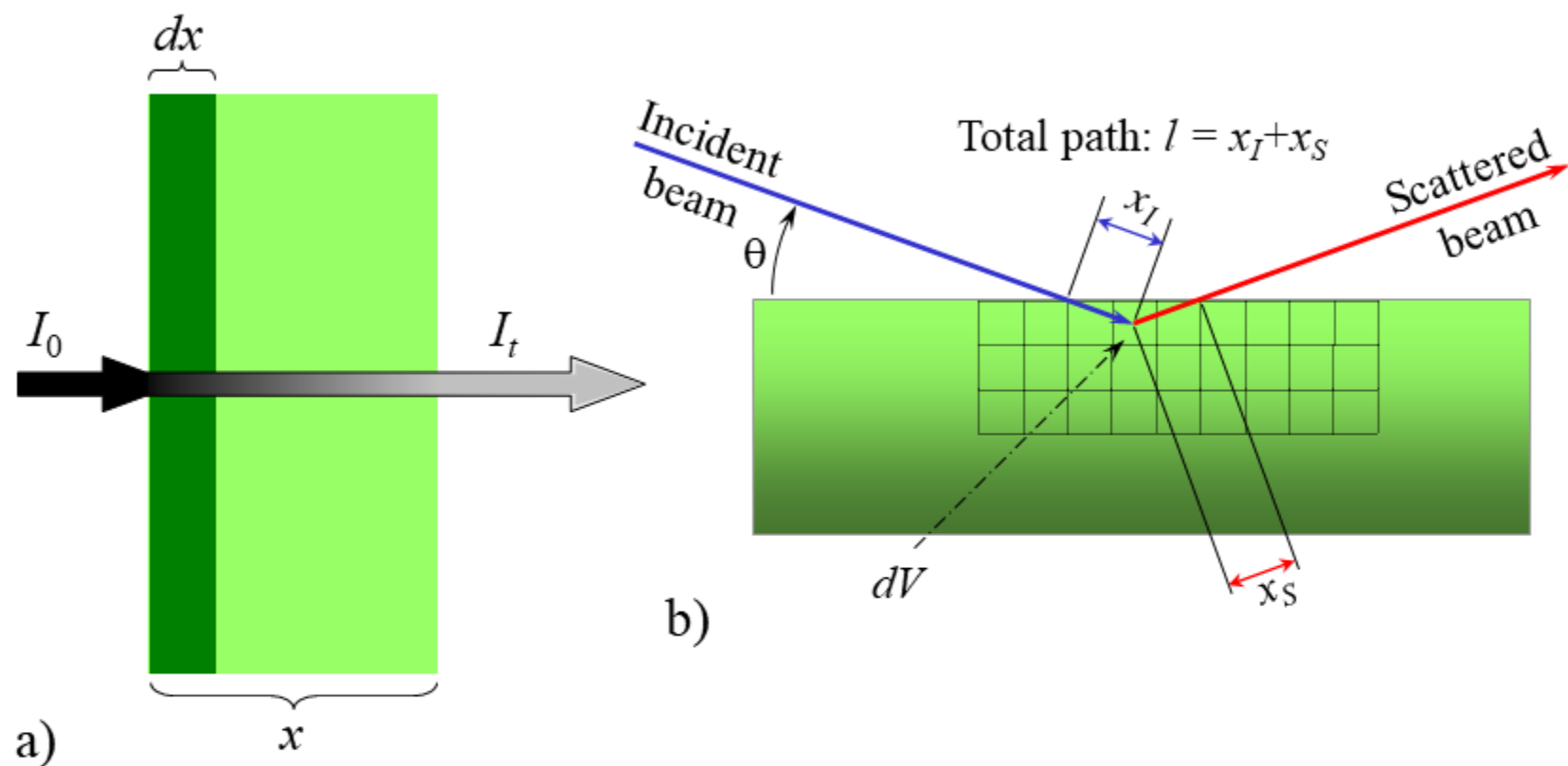
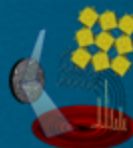


Figure 8.18. Lorentz-polarization factor as a function of Bragg angle: the solid line represents calculation using Eq. 8.46 (no monochromator), and the dash-dotted line is calculated assuming graphite monochromator and Cu $K\alpha$ radiation with $K = 0.5$ (Eq. 8.47).

$$LP = \frac{1 + \cos^2 2\theta \cos^2 2\theta}{\cos \theta \cdot \sin^2 \theta} \quad \text{Eq. 8.47}$$



Eq. 8.51.

$$A = \frac{1}{V} \int_V \exp(-\mu_{\text{eff}} l) dV$$

Eq. 8.53.

$$A = 1 - \exp(-2\mu_{\text{eff}} t / \sin \theta)$$

Figure 8.19. Schematic explaining the phenomenon of absorption of X-rays by the matter (a) and the illustration of the derivation of Eq. 8.51 (b). The incident beam penetrates into the sample by the distance x_I before being scattered by the infinitesimal volume dV . The scattered beam traverses the distance x_S before exiting the sample. In the Bragg–Brentano geometry $x_I = x_S$.

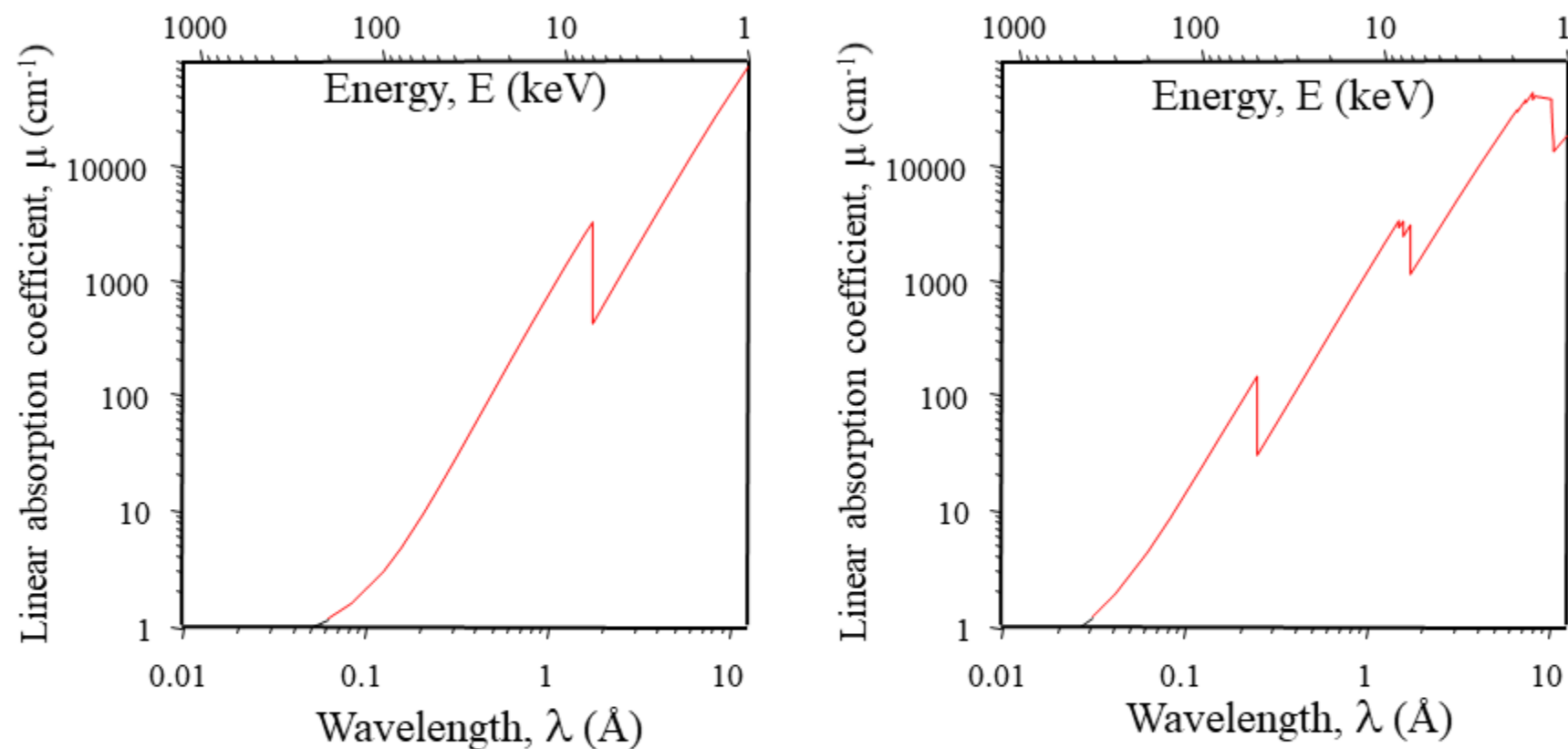
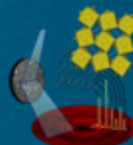


Figure 8.20. The behavior of the linear absorption coefficients of the elemental iron (*left*) and gadolinium (*right*) as functions of the wavelength of the X-rays (*bottom scale*) and photon energy (*top scale*). The numerical data used to prepare both plots have been taken from the National Institute of Standards and Technology Physical Reference Data web page.

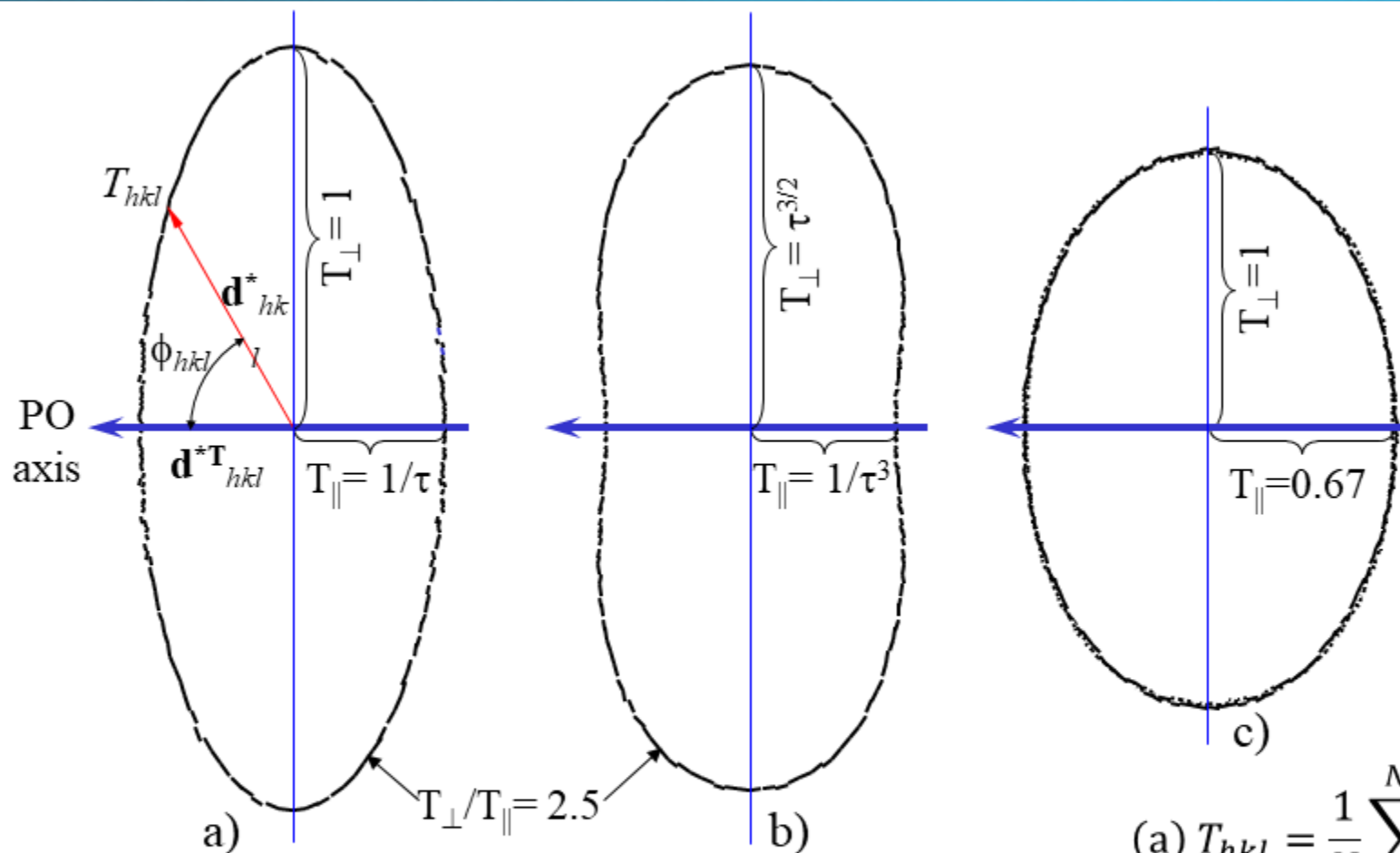
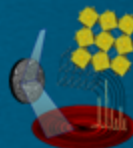
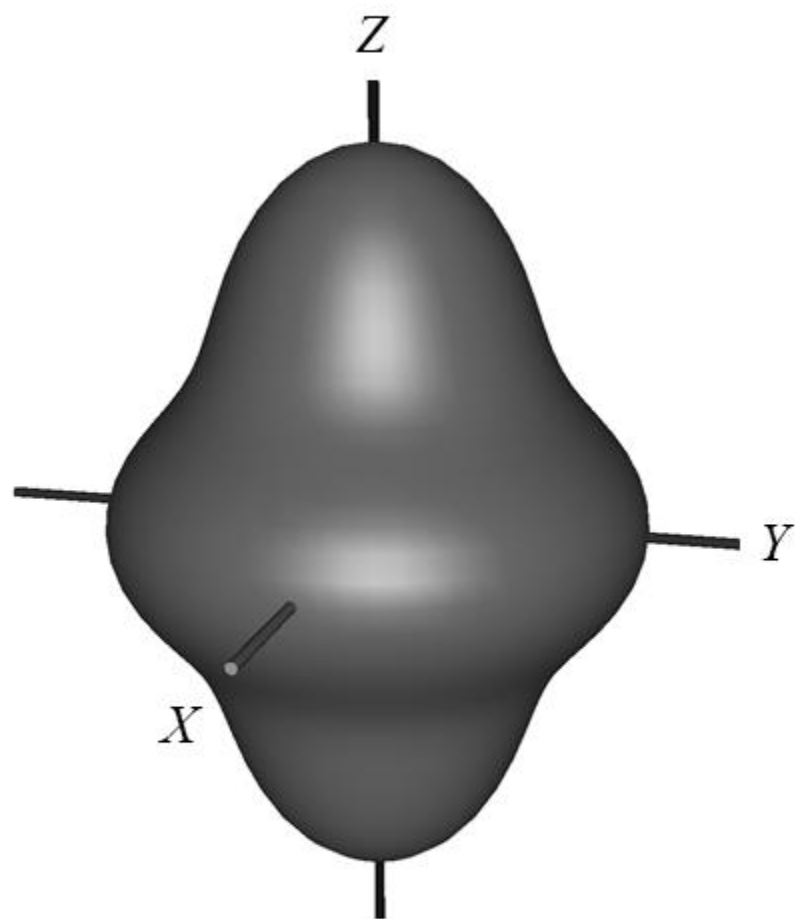


Figure 8.21. Preferred orientation functions for needles represented by the ellipsoidal (a) and March-Dollase (b) functions with the magnitude $T_{\perp}/T_{\parallel} = 2.5$, and the two functions overlapped when $T_{\perp}/T_{\parallel} = 1.5$ (c). The two notations, $T_{\parallel}$ and $T_{\perp}$, refer to preferred orientation corrections in the directions parallel and perpendicular to the preferred orientation (PO) axis, respectively.

$$(a) T_{hkl} = \frac{1}{N} \sum_{i=1}^N [1 + (\tau^2 - 1) \cos^2 \phi_{hkl}^i]^{-1/2} \quad \text{Eq. 8.57}$$

$$(b) T_{hkl} = \frac{1}{N} \sum_{i=1}^N \left(\tau^2 \cos^2 \phi_{hkl}^i + \frac{1}{\tau} \sin^2 \phi_{hkl}^i \right)^{-3/2} \quad \text{Eq. 8.58}$$



Preferred Orientation Correction $T(h)$ and Magnitude J :

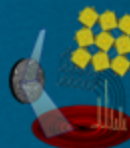
$$T(h) = 1 + \sum_{l=2}^L \frac{4\pi}{2l+1} \sum_{m=-l}^l C_l^m k_l^m(h) \quad \text{Eq. 8.62}$$

where:

- h represents reflection orientations;
- L is the maximum order of a harmonic;
- C_l^m are harmonic coefficients;
-

$$J = 1 + \sum_{l=2}^L \frac{1}{2l+1} \sum_{m=-l}^l |C_l^m|^2 \quad \text{Eq. 8.63}$$

Figure 8.22. The illustration of the complex distribution of reciprocal lattice vectors modeled using a **spherical harmonic preferred orientation** function for the (100) reflection.



Extinction Factor:

$$E_{hkl} = E_B \sin^2 \theta + E_L \cos^2 \theta \quad \text{Eq. 8. 64}$$

where: E_B and E_L are Bragg ($2\theta = \pi$) and Laue ($2\theta = 0$) components.

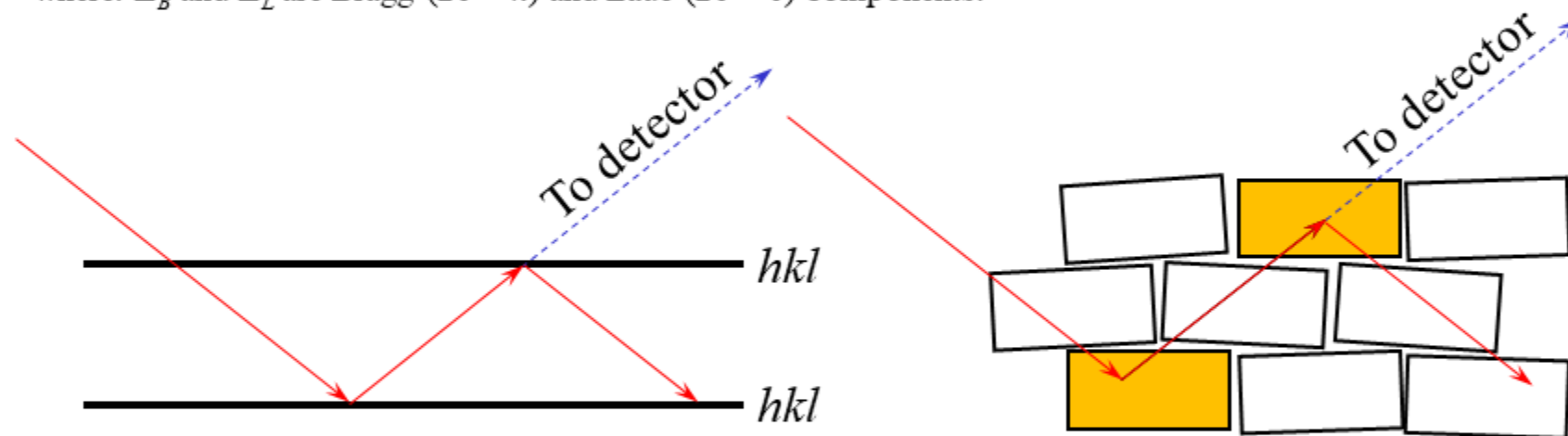


Figure 8.23. The illustration of primary (*left*) and secondary (*right*) extinction effects, which reduce the intensity of strong reflections from perfect crystals and ideally mosaic crystals, respectively. The solid red lines indicate actual reflections paths, while the dashed blue lines indicate the expected paths that are partially suppressed by dynamical effects. The orange rectangles on the right indicate two different blocks of mosaic with identical orientations.