

Fourier Transformation:

$$\Phi(\mathbf{h}) = \int_V \rho(\mathbf{x}) \exp[2\pi i(\mathbf{h} \cdot \mathbf{x})] d^3\mathbf{x} \quad \text{Eq. 10.1}$$

$$\rho(\mathbf{x}) = \int_{V^*} \Phi(\mathbf{h}) \exp[-2\pi i(\mathbf{h} \cdot \mathbf{x})] d^3\mathbf{h} \quad \text{Eq. 10.2}$$

$$\mathbf{F}(\mathbf{h}) = V \sum_{\mathbf{x}} \rho(\mathbf{x}) \exp[2\pi i(\mathbf{h} \cdot \mathbf{x})] \quad \text{Eq. 10.3}$$

$$\rho(\mathbf{x}) = \frac{1}{V} \sum_{\mathbf{h}} \mathbf{F}(\mathbf{h}) \exp[-2\pi i(\mathbf{h} \cdot \mathbf{x})] \quad \text{Eq. 10.4}$$

$$\rho_{xyz} = \frac{1}{V} \sum_{h=-\infty}^{h=+\infty} \sum_{k=-\infty}^{k=+\infty} \sum_{l=-\infty}^{l=+\infty} \mathbf{F}_{hkl} \exp[-2\pi i(hx + ky + lz)] \quad \text{Eq. 10.5}$$

$$\Delta\rho_{xyz} = \frac{1}{V} \sum_{h=-\infty}^{h=+\infty} \sum_{k=-\infty}^{k=+\infty} \sum_{l=-\infty}^{l=+\infty} (\mathbf{F}_{hkl}^{obs} - \mathbf{F}_{hkl}^{calc}) \exp[-2\pi i(hx + ky + lz)] \quad \text{Eq. 10.8}$$

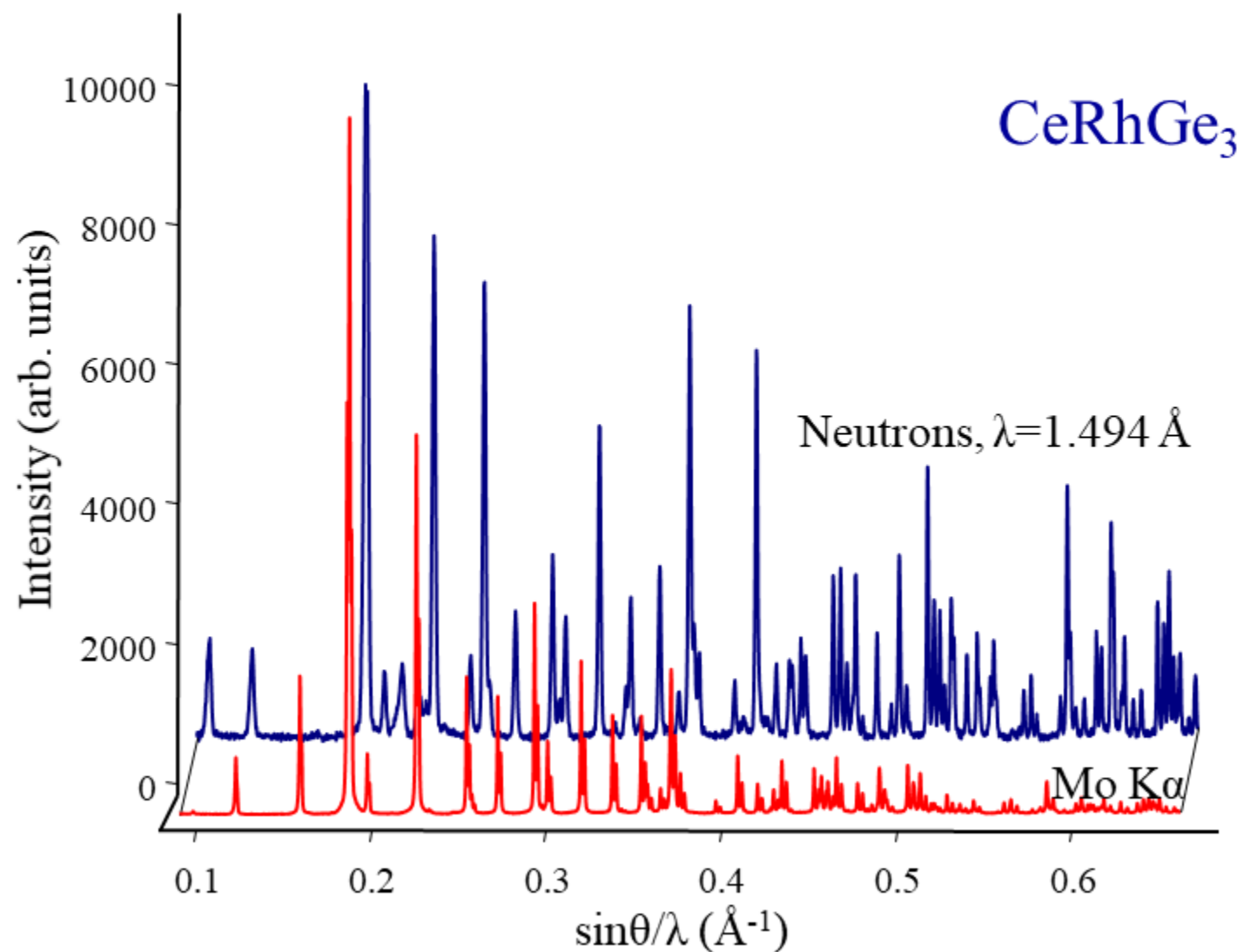
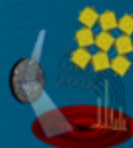


Figure 10.1. Two powder diffraction patterns of the intermetallic compound CeRhGe_3 . The *bottom plot* depicts X-ray data collected using Mo $K\alpha$ radiation at room temperature, and the *top plot* displays neutron diffraction data collected at $T = 200 \text{ K}$, using thermal neutrons with $\lambda = 1.494 \text{ \AA}$.

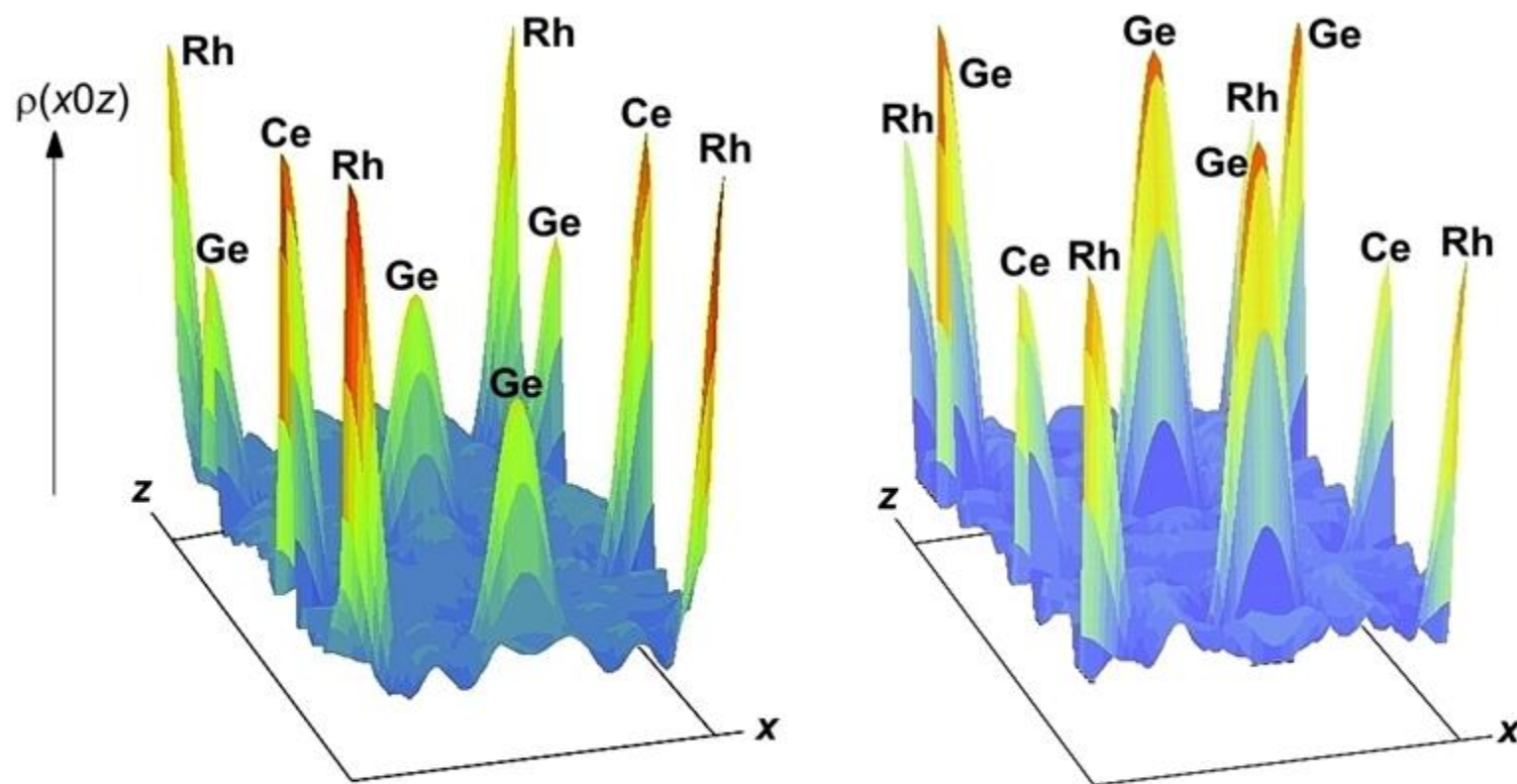
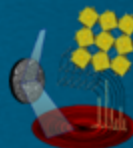


Figure 10.2. The electron (*left*) and nuclear (*right*) density distributions in the $x0z$ plane of the unit cell of CeRhGe_3 calculated from X-ray and neutron powder diffraction data, respectively (Figure 10.1). The contour of the unit cell is shown schematically as the rectangle under each Fourier map. The peaks correspond to various atoms located in this plane and are so labeled on the figure. The volumes of the peaks are proportional to the scattering ability of atoms: for X-ray, the scattering power decreases in the series $\text{Ce}(58e) \rightarrow \text{Rh}(45e) \rightarrow \text{Ge}(32e)$; for neutrons, the coherent scattering lengths decrease in the reverse order: $\text{Ge}(8.19 \text{ fm}) \rightarrow \text{Rh}(5.88 \text{ fm}) \rightarrow \text{Ce}(4.84 \text{ fm})$.



Patterson Function or Heavy Atom Method:

$$P_{uvw} = \frac{2}{V} \sum_{h=0}^{h=+\infty} \sum_{k=-\infty}^{k=+\infty} \sum_{l=-\infty}^{l=+\infty} |\mathbf{F}_{hkl}^{obs}|^2 \cos[2\pi(hu + kv + lw)] \quad \text{Eq. 10.9}$$

Peaks Height:

$$H_{ij} \propto Z_i Z_j$$

Eq. 10.12

Table 10.1. Interatomic vectors (shown in bold) produced by an atom located in the general site position in the monoclinic crystal system, space group $P2_1/m$.

Symmetry element	Symmetry operation	x, y, z	$-x, \frac{1}{2}+y, -z$	$-x, -y, -z$	$x, \frac{1}{2}-y, z$
1	x, y, z	$0, 0, 0$	$2x, \frac{1}{2}, 2z$	$2x, 2y, 2z$	$0, -\frac{1}{2}+2y, 0$
2_1	$-x, \frac{1}{2}+y, -z$	$-2x, \frac{1}{2}, -2z$	$0, 0, 0$	$0, \frac{1}{2}+2y, 0$	$-2x, 2y, -2z$
-1	$-x, -y, -z$	$-2x, -2y, -2z$	$0, -\frac{1}{2}-2y, 0$	$0, 0, 0$	$-2x, -\frac{1}{2}, -2z$
m	$x, \frac{1}{2}-y, z$	$0, \frac{1}{2}-2y, 0$	$2x, -2y, 2z$	$2x, \frac{1}{2}, 2z$	$0, 0, 0$

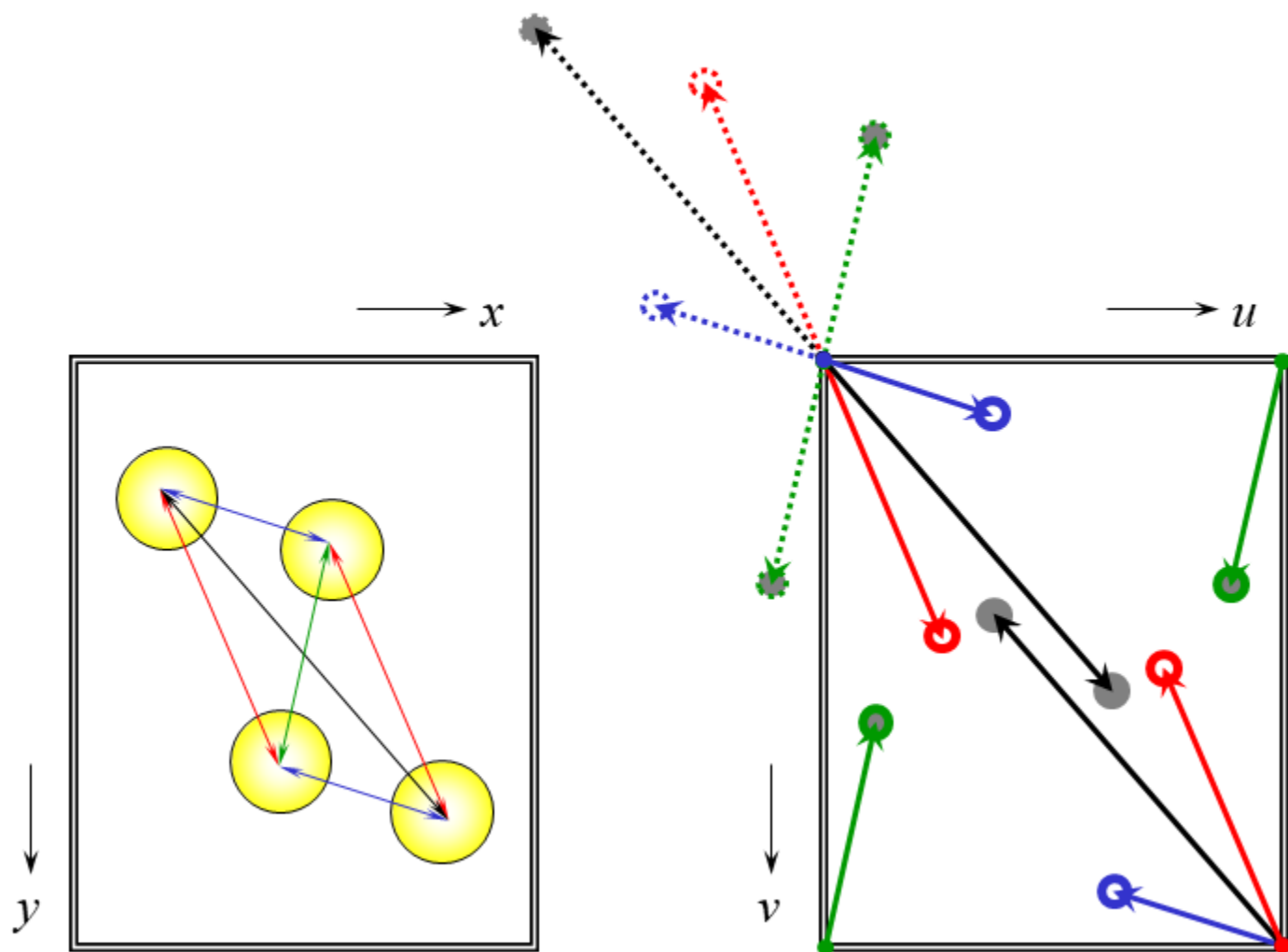
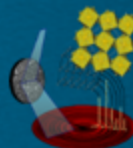


Figure 10.3. The relationships between the distribution of atoms (*left*), and the Patterson function (*right*) in a two-dimensional unit cell. All possible interatomic vectors are drawn on the left. On the right, they are brought to a common origin (*upper left corner*) of the unit cell. Vectors that are outside the unit cell are shown using dotted lines. The content of one unit cell in the Patterson space (*right*) is shown using solid lines. *Blue and red circles* depict a two-fold increase in the height of the corresponding peaks of the Patterson function when compared with those marked using *grey and green circles*, which occurs due to a complete overlap of vectors coinciding with the parallel sides of the parallelogram of atoms on the *left*.

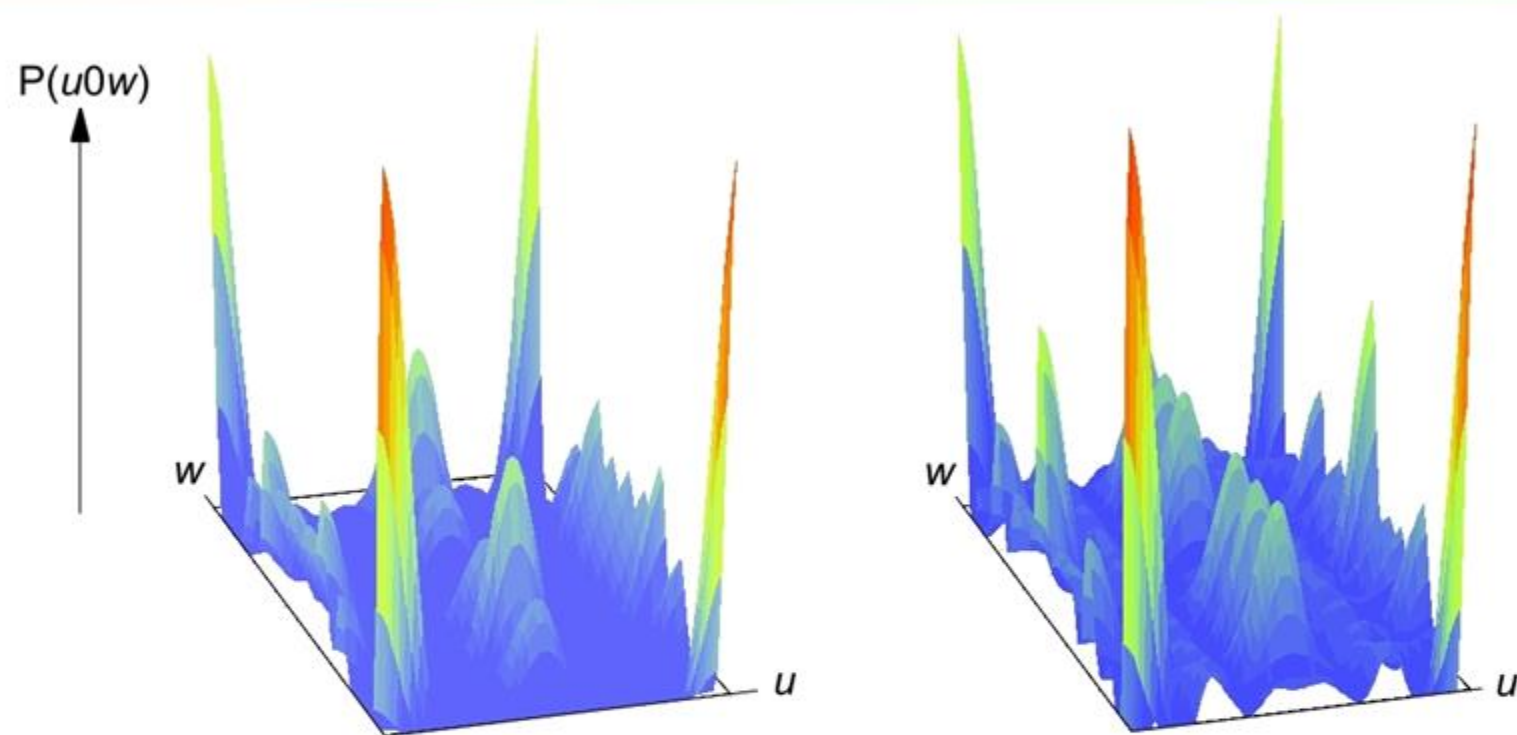
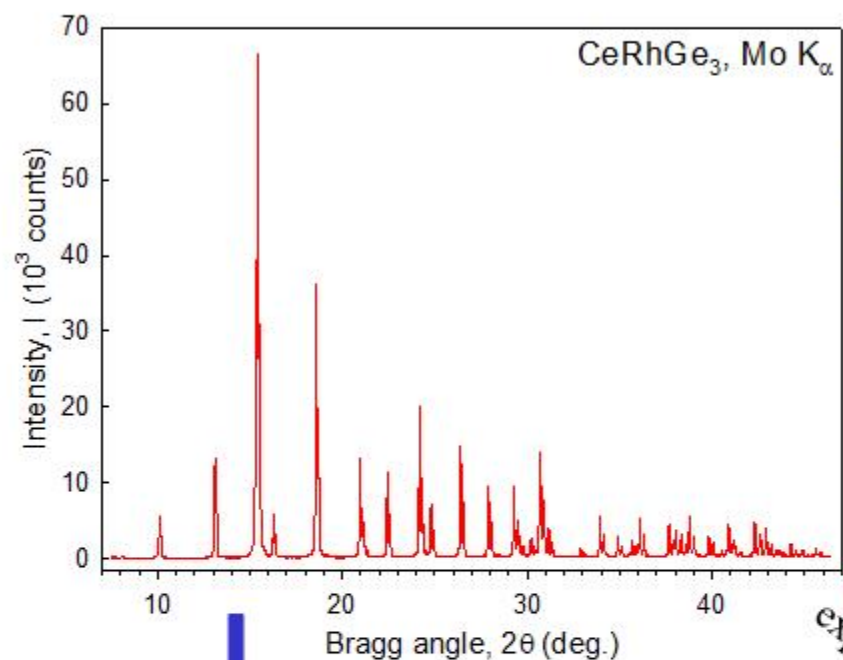


Figure 10.4. Patterson functions calculated in the $u0w$ plane using Eq. 10.9 and employing experimental X-ray (*left*) and neutron (*right*) powder diffraction data shown in Figure 10.1. The strongest peak in any Patterson function is always observed at $(0, 0, 0)$ because the origins of all vectors coincide with the origin of coordinates. In this example, since the real crystal structure contains an atom at $(0, 0, 0)$, some of the peaks on the Patterson map correspond to the actual locations of atoms (i.e., $\mathbf{u}^j = \mathbf{x}^j \pm 0$). The contour of the unit cell is shown schematically as the rectangle beneath each Patterson map.



Individual Bragg reflections
 Unit cell dimensions, content, symmetry
 Fourier transformation - Patterson
 Model of the crystal structure
 Fourier transformation - Electron density

Individual Bragg reflections
 Unit cell dimensions, content, symmetry
 Normalized structure amplitudes
 Direct phase determination
 Fourier transformation - E-map
 Model of the crystal structure
 Fourier transformation - Electron density

Diffraction experiment

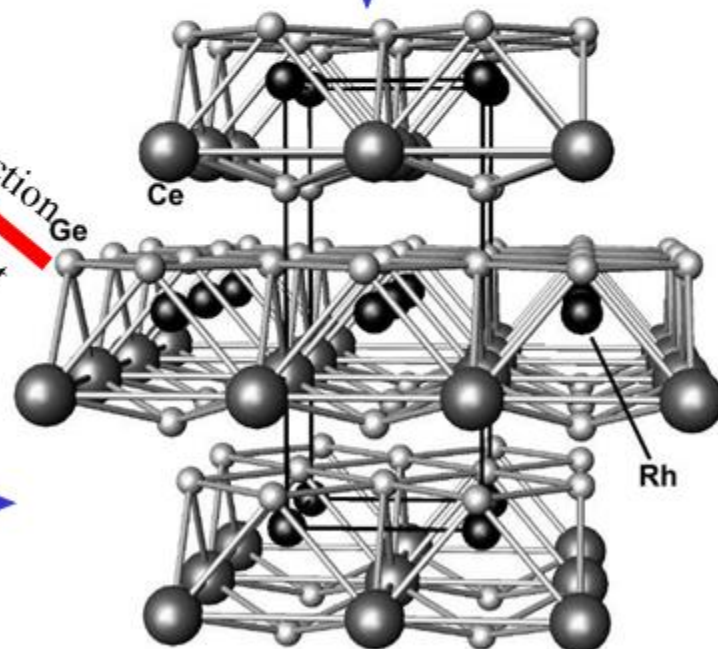
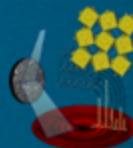


Figure 10.5. The schematic illustrating how the powder diffraction pattern (*top left*) can be transformed into the image of the crystal structure in three dimensions (*bottom right*). Both the diffraction pattern and the model of the crystal structure represent the intermetallic compound CeRhGe_3 .



Direct Methods:

Triples are defined as follows:

$$\begin{array}{lll} \text{First reflection,} & \mathbf{h} & : h, k, l \\ \text{Second reflection,} & \mathbf{h}' & : h', k', l' \\ \text{Third reflection,} & \mathbf{h} - \mathbf{h}' & : h - h', k - k', l - l' \end{array} \quad \text{Eq. 10.13}$$

Signs relationship in Triples :

$$S_{\mathbf{h}} \approx S_{\mathbf{h}'} S_{\mathbf{h}-\mathbf{h}'} \quad \text{Eq. 10.16}$$

Normalized structure factor:

$$E_{hkl} = \frac{|\mathbf{F}_{hkl}|}{\langle F_{\text{exp}}^2 \rangle^{1/2}} \quad \text{Eq. 10.14} \quad \langle F_{\text{exp}}^2 \rangle = \sum_{j=1}^n f_j^2(s) \quad \text{Eq. 10.15}$$

Probability of Sign (Phase) in:

$$P_+ = 1/2 + 1/2 \tanh[N^{-1/2} |E_{\mathbf{h}}| E_{\mathbf{h}'} E_{\mathbf{h}-\mathbf{h}'}] \quad \text{Eq. 10.17}$$

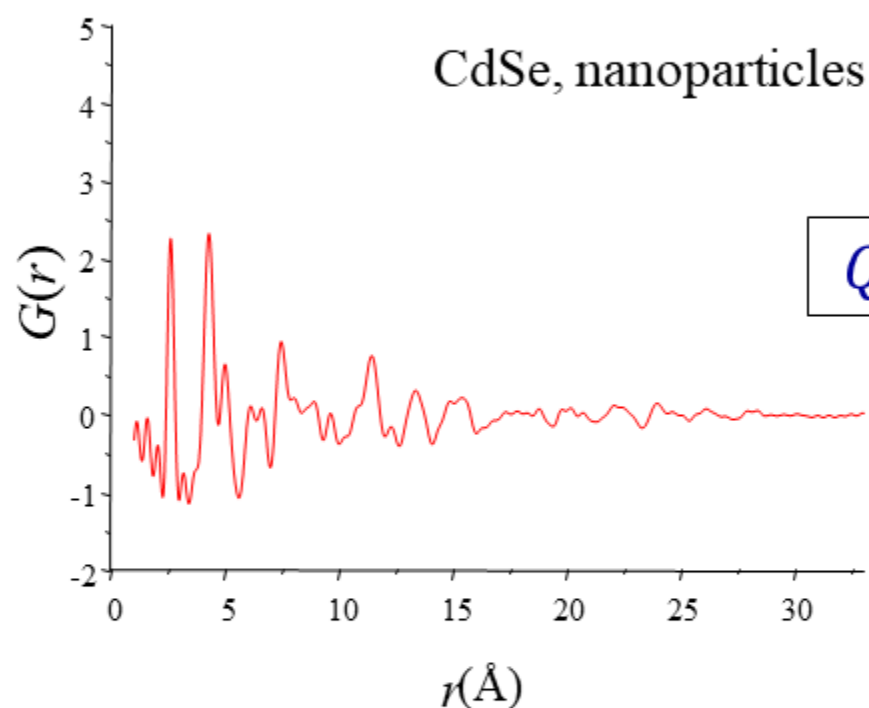
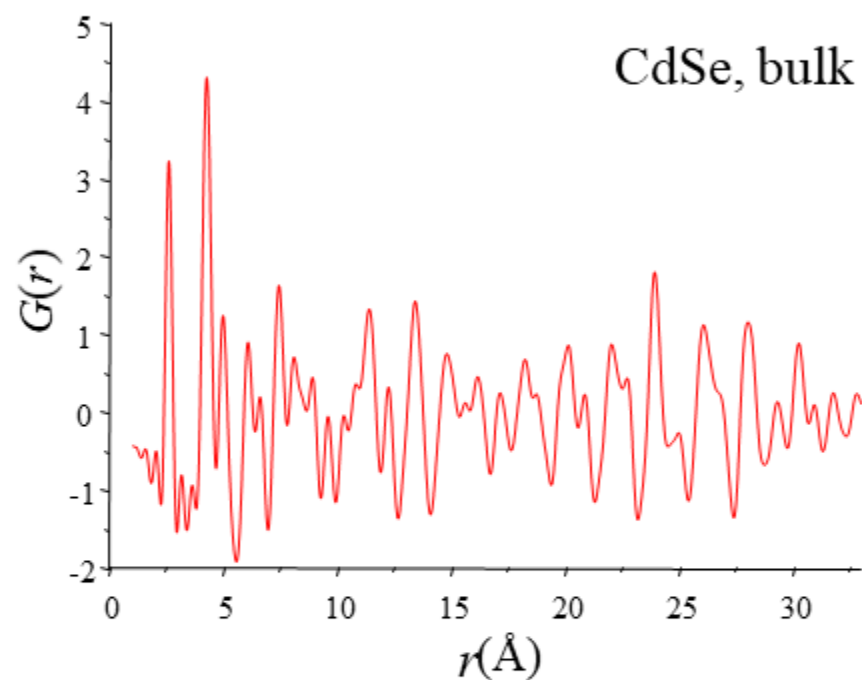
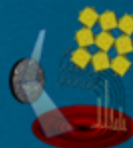
$$P_{\alpha_{\mathbf{h}}} = \frac{1}{2\pi I_0(k_{\mathbf{h},\mathbf{h}'})} \exp[k_{\mathbf{h},\mathbf{h}'} \cos(\alpha_{\mathbf{h}'} + \alpha_{\mathbf{h}-\mathbf{h}'})] \quad \text{Eq. 10.20}$$

Tangent Formula:

$$\tan \alpha_{\mathbf{h}} \cong \frac{\sum_{\mathbf{h}'} |E_{\mathbf{h}'}| |E_{\mathbf{h}-\mathbf{h}'}| \sin(\alpha_{\mathbf{h}'} + \alpha_{\mathbf{h}-\mathbf{h}'})}{\sum_{\mathbf{h}'} |E_{\mathbf{h}'}| |E_{\mathbf{h}-\mathbf{h}'}| \cos(\alpha_{\mathbf{h}'} + \alpha_{\mathbf{h}-\mathbf{h}'})} \quad \text{Eq. 10.21}$$

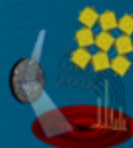
Electron Density:

$$\rho_{xyz} = \frac{1}{V} \sum_{h=-\infty}^{h=+\infty} \sum_{k=-\infty}^{k=+\infty} \sum_{l=-\infty}^{l=+\infty} E_{hkl} \cos[2\pi \mathbf{i}(hx + ky + lz - \alpha_{hkl}^{\text{direct}})] \quad \text{Eq. 10.22}$$



$$Q = |\mathbf{Q}| = 4\pi \sin(\theta)/\lambda$$

Figure 10.6. Experimental **pair distribution function** of CdSe from bulk material (*left*) and 30 Å nanoparticles (*right*). Numerical data used to produce these plots were taken from the DIFFpy tutorial.



Total Scattering Analysis Using Pair Distribution Function:

Function of interatomic distance:
$$I(Q) = \sum_{i=1}^N \sum_{j=1}^N f_i f_j \frac{\sin(Qr_{ij})}{Qr_{ij}}$$
 Eq. 10.23

Reduced structural function
$$F(Q) = Q \times \frac{I^{\text{coh}}(Q) - \sum c_i |f_i(Q)|^2}{\sum c_i |f_i(Q)|^2}$$
 Eq. 10.25

Reduced pair distribution function:
$$G(r) = 4\pi r [\rho(r) - \rho_0] = 4\pi r \rho_0 [g(r) - 1]$$
 Eq. 10.26

Atomic pair density:
$$\rho(r) = \frac{1}{4\pi r^2 N} \sum_i^N \sum_{j \neq i}^N \frac{f_i f_j}{\langle f \rangle^2} \delta(r - r_{ij})$$
 Eq. 10.27

Calculated $G(r)$ function:
$$G_{\text{calc}}(r) = \frac{1}{rN} \sum_i^N \sum_{j \neq i}^N \left[\frac{f_i f_j}{\langle f \rangle^2} \delta(r - r_{ij}) \right] - 4\pi r \rho_0$$
 Eq. 10.28

The minimized function:
$$\Phi = \sum_{i=1}^N w_i \left(G^{\text{calc}}(r_i) - G^{\text{obs}}(r_i) \right)^2$$
 Eq. 10.29