

## 4. DIFFUSE SCATTERING AND RELATED TOPICS

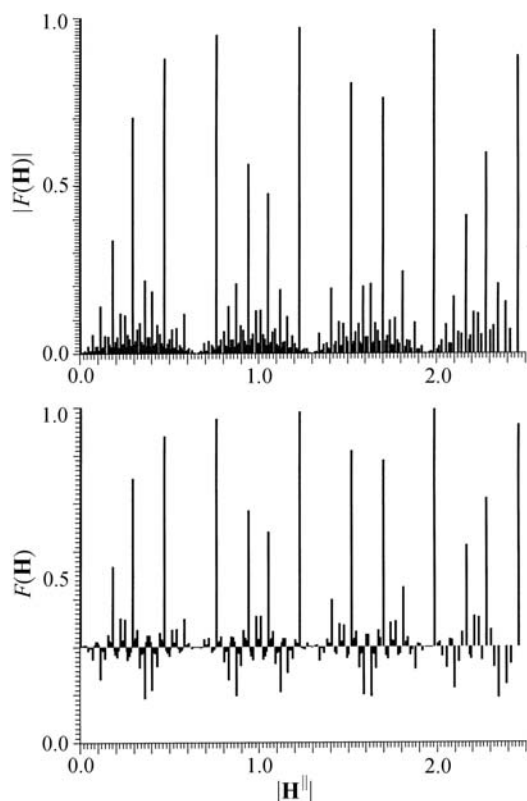


Fig. 4.6.3.5. The structure factors  $F(\mathbf{H})$  (below) and their magnitudes  $|F(\mathbf{H})|$  (above) of a Fibonacci chain decorated with equal point atoms are shown as a function of the parallel-space component  $|\mathbf{H}^{\parallel}|$  of the diffraction vector. The short distance in the Fibonacci chain is  $S = 2.5 \text{ \AA}$ , all structure factors within  $0 \leq |\mathbf{H}| \leq 2.5 \text{ \AA}^{-1}$  have been calculated and normalized to  $F(00) = 1$ .

function of  $\mathbf{H}^{\perp}$  (Fig. 4.6.3.6), ‘neighbouring’ reflections of strong Bragg peaks are extremely weak and, consequently, the reciprocal space appears to be filled with *discrete* Bragg peaks even for low-resolution experiments.

This property allows an unambiguous identification of a correct set of reciprocal-basis vectors. However, infinitely many sets allowing a correct indexing of the diffraction pattern with integer indices exist. Nevertheless, an optimum basis (low indices are assigned to strong reflections) can be derived: the intensity distribution, not the metrics, characterizes the best choice of indexing. Once the minimum distance  $S$  in the structure is identified from chemical considerations, the reciprocal basis should be chosen as described in Section 4.6.2.4. It has to be kept in mind, however, that the identification of the metrics is not sufficient to distinguish in the 1D aperiodic case between an incommensurately modulated structure, a quasiperiodic structure or special kinds of structures with fractally shaped atomic surfaces.

A correct set of reciprocal-basis vectors can be identified in the following way:

- (1) Find pairs of strong reflections whose physical-space diffraction vectors are related to each other by the factor  $\tau$ .
- (2) Index these reflections by assigning an appropriate value to  $a^*$ . This value should be derived from the shortest interatomic distance  $S$  expected in the structure.
- (3) The reciprocal basis is correct if all observable Bragg reflections can be indexed with integer numbers.

## 4.6.3.3.1.2. Diffraction symmetry

The possible Laue symmetry group  $K^{3D}$  of the Fourier module  $M^* = \{\mathbf{H}^{\parallel} = \sum_{i=1}^4 h_i \mathbf{a}_i^* | h_i \in \mathbb{Z}\}$  is any one of the direct product  $K^{3D} = K^{2D} \otimes K^{1D} \otimes 1$ .  $K^{2D}$  corresponds to one of the ten crystallographic 2D point groups,  $K^{1D} = \{1\}$  in the general case of a quasiperiodic stacking of periodic layers. Consequently, the nine Laue groups  $\bar{1}, 2/m, mmm, 4/m, 4/mmm,$

$\bar{3}, \bar{3}m, 6/m$  and  $6/mmm$  are possible. These are all 3D crystallographic Laue groups except for the two cubic ones.

The (unweighted) Fourier module shows only 2D lattice symmetry. In the third dimension, the submodule  $M_1^*$  remains invariant under the scaling symmetry operation  $S^n M_1^* = \tau^n M_1^*$  with  $n \in \mathbb{Z}$ . The scaling symmetry operators  $S^n$  form an infinite group  $s = \{\dots, S^{-1}, S^0, S^1, \dots\}$  of reciprocal-basis transformations  $S^n$  in superspace,

$$S^n = \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}_D^n, \quad S^{-1} = \begin{pmatrix} \bar{1} & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}_D,$$

$$S^0 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}_D,$$

and act on the reciprocal basis  $\mathbf{d}_i^*$  in superspace.

## 4.6.3.3.1.3. Structure factor

The structure factor of a periodic structure is defined as the Fourier transform of the density distribution  $\rho(\mathbf{r})$  of its unit cell (UC):

$$F(\mathbf{H}) = \int_{\text{UC}} \rho(\mathbf{r}) \exp(2\pi i \mathbf{H} \cdot \mathbf{r}) \, d\mathbf{r}.$$

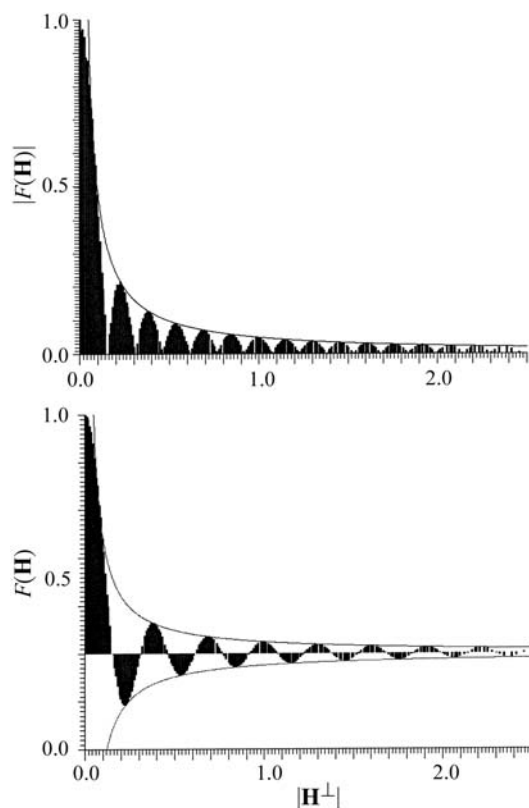


Fig. 4.6.3.6. The structure factors  $F(\mathbf{H})$  (below) and their magnitudes  $|F(\mathbf{H})|$  (above) of a Fibonacci chain decorated with equal point atoms are shown as a function of the perpendicular-space component  $|\mathbf{H}^{\perp}|$  of the diffraction vector. The short distance in the Fibonacci chain is  $S = 2.5 \text{ \AA}$ , all structure factors within  $0 \leq |\mathbf{H}| \leq 2.5 \text{ \AA}^{-1}$  have been calculated and normalized to  $F(00) = 1$ .

#### 4.6. RECIPROCAL-SPACE IMAGES OF APERIODIC CRYSTALS

The same is valid in the case of the  $nD$  description of a quasi-periodic structure. The parallel- and perpendicular-space components are orthogonal to each other and can be separated. In the case of the 1D Fibonacci sequence, the Fourier transform of the parallel-space component of the electron-density distribution of a single atom gives the usual atomic scattering factor  $f(\mathbf{H}^{\parallel})$ . Parallel to  $x^{\perp}$ ,  $\rho(\mathbf{r})$  adopts values  $\neq 0$  only within the interval  $-(1+\tau)/[2a^*(2+\tau)] \leq x^{\perp} \leq (1+\tau)/[2a^*(2+\tau)]$  and one obtains

$$F(\mathbf{H}) = f(\mathbf{H}^{\parallel})[a^*(2+\tau)]/(1+\tau) \times \int_{-(1+\tau)/[2a^*(2+\tau)]}^{+(1+\tau)/[2a^*(2+\tau)]} \exp(2\pi i \mathbf{H}^{\perp} \cdot x^{\perp}) dx^{\perp}.$$

The factor  $[a^*(2+\tau)]/(1+\tau)$  results from the normalization of the structure factors to  $F(\mathbf{0}) = f(0)$ . With

$$\begin{aligned} \mathbf{H} &= h_1 \mathbf{d}_1^* + h_2 \mathbf{d}_2^* + h_3 \mathbf{d}_3^* + h_4 \mathbf{d}_4^* \\ &= h_1 a_1^* \begin{pmatrix} 1 \\ -\tau \\ 0 \\ 0 \end{pmatrix} + h_2 a_1^* \begin{pmatrix} \tau \\ 1 \\ 0 \\ 0 \end{pmatrix} + h_3 a_3^* \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \end{pmatrix} + h_4 a_4^* \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix} \end{aligned}$$

and  $\mathbf{H}^{\perp} = a_1^*(-\tau h_1 + h_2)$  the integrand can be rewritten as

$$F(\mathbf{H}) = f(\mathbf{H}^{\parallel})[a^*(2+\tau)]/(1+\tau) \times \int_{-(1+\tau)/[2a^*(2+\tau)]}^{+(1+\tau)/[2a^*(2+\tau)]} \exp[2\pi i(-\tau h_1 + h_2)x^{\perp}] dx^{\perp},$$

yielding

$$F(\mathbf{H}) = f(\mathbf{H}^{\parallel})(2+\tau)/[2\pi i(-\tau h_1 + h_2)(1+\tau)] \times \exp[2\pi i(-\tau h_1 + h_2)x^{\perp}] \Big|_{-(1+\tau)/[2a^*(2+\tau)]}^{+(1+\tau)/[2a^*(2+\tau)]}.$$

Using  $\sin x = (e^{ix} - e^{-ix})/2i$  gives

$$F(\mathbf{H}) = f(\mathbf{H}^{\parallel})(2+\tau)/[\pi(-\tau h_1 + h_2)(1+\tau)] \times \sin[\pi(1+\tau)(-\tau h_1 + h_2)]/(2+\tau).$$

Thus, the structure factor has the form of the function  $\sin(x)/x$  with  $x$  a perpendicular reciprocal-space coordinate. The upper and lower limiting curves of this function are given by the hyperbolae  $\pm 1/x$  (Fig. 4.6.3.6). The continuous shape of  $F(\mathbf{H})$  as a function of  $\mathbf{H}^{\perp}$  allows the estimation of an overall temperature factor and atomic scattering factor for reflection-data normalization (compare Figs. 4.6.3.6 and 4.6.3.7).

In the case of a 3D crystal structure which is quasiperiodic in one direction, the structure factor can be written in the form

$$F(\mathbf{H}) = \sum_{k=1}^n [T_k(\mathbf{H}) f_k(\mathbf{H}^{\parallel}) g_k(\mathbf{H}^{\perp}) \exp(2\pi i \mathbf{H} \cdot \mathbf{r}_k)].$$

The sum runs over all  $n$  averaged hyperatoms in the 4D unit cell of the structure. The *geometric form factor*  $g_k(\mathbf{H}^{\perp})$  corresponds to the Fourier transform of the  $k$ th atomic surface,

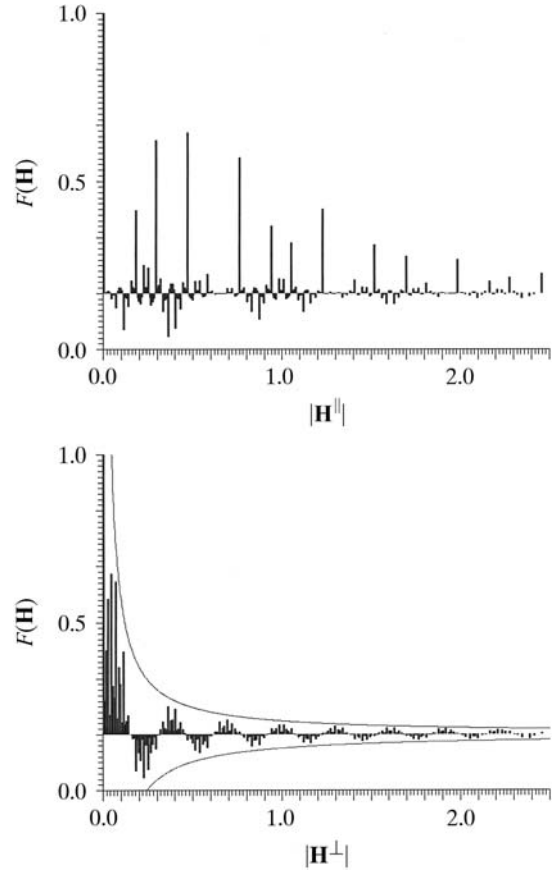


Fig. 4.6.3.7. The structure factors  $F(\mathbf{H})$  of the Fibonacci chain decorated with aluminium atoms ( $U_{\text{overall}} = 0.005 \text{ \AA}^2$ ) as a function of the parallel (above) and the perpendicular (below) component of the diffraction vector. The short distance is  $S = 2.5 \text{ \AA}$ , all structure factors within  $0 \leq |\mathbf{H}| \leq 2.5 \text{ \AA}^{-1}$  have been calculated and normalized to  $F(00) = 1$ .

$$g_k(\mathbf{H}^{\perp}) = (1/A_{\text{UC}}^{\perp}) \int_{A_k} \exp(2\pi i \mathbf{H}^{\perp} \cdot \mathbf{r}^{\perp}) d\mathbf{r}^{\perp},$$

normalized to  $A_{\text{UC}}^{\perp}$ , the area of the 2D unit cell projected upon  $\mathbf{V}^{\perp}$ , and  $A_k$ , the area of the  $k$ th atomic surface.

The atomic temperature factor  $T_k(\mathbf{H})$  can also have perpendicular-space components. Assuming only harmonic (static or dynamic) displacements in parallel and perpendicular space one obtains, in analogy to the usual expression (Willis & Pryor, 1975),

$$\begin{aligned} T_k(\mathbf{H}) &= T_k(\mathbf{H}^{\parallel}, \mathbf{H}^{\perp}) \\ &= \exp(-2\pi^2 \mathbf{H}^{\parallel T} \langle \mathbf{u}_i^{\parallel} \mathbf{u}_j^{\parallel T} \rangle \mathbf{H}^{\parallel}) \exp(-2\pi^2 \mathbf{H}^{\perp T} \langle \mathbf{u}_i^{\perp} \mathbf{u}_j^{\perp T} \rangle \mathbf{H}^{\perp}), \end{aligned}$$

with

$$\langle \mathbf{u}_i^{\parallel} \mathbf{u}_j^{\parallel T} \rangle = \begin{pmatrix} \langle \mathbf{u}_1^{\parallel 2} \rangle & \langle \mathbf{u}_1^{\parallel} \cdot \mathbf{u}_2^{\parallel T} \rangle & \langle \mathbf{u}_1^{\parallel} \cdot \mathbf{u}_3^{\parallel T} \rangle \\ \langle \mathbf{u}_2^{\parallel} \cdot \mathbf{u}_1^{\parallel T} \rangle & \langle \mathbf{u}_2^{\parallel 2} \rangle & \langle \mathbf{u}_2^{\parallel} \cdot \mathbf{u}_3^{\parallel T} \rangle \\ \langle \mathbf{u}_3^{\parallel} \cdot \mathbf{u}_1^{\parallel T} \rangle & \langle \mathbf{u}_3^{\parallel} \cdot \mathbf{u}_2^{\parallel T} \rangle & \langle \mathbf{u}_3^{\parallel 2} \rangle \end{pmatrix}$$

and  $\langle \mathbf{u}_i^{\perp} \mathbf{u}_j^{\perp T} \rangle = \langle \mathbf{u}_i^{\perp 2} \rangle$ .

The elements of the type  $\langle \mathbf{u}_i \cdot \mathbf{u}_j^T \rangle$  represent the average values of the atomic displacements along the  $i$ th axis times the displacement along the  $j$ th axis on the  $V$  basis.

##### 4.6.3.3.1.4. Intensity statistics

In the following, only the properties of the quasiperiodic component of the 3D structure, namely the Fourier module  $M_1^*$ ,