

Programming incommensurately

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A revolutionary proposal

- **Rhombohedral space groups** are notoriously difficult to deal with.
- Their symmetry properties are different from other crystals, and require special handling
- They account only for about 1% of all structures (according to CSD)

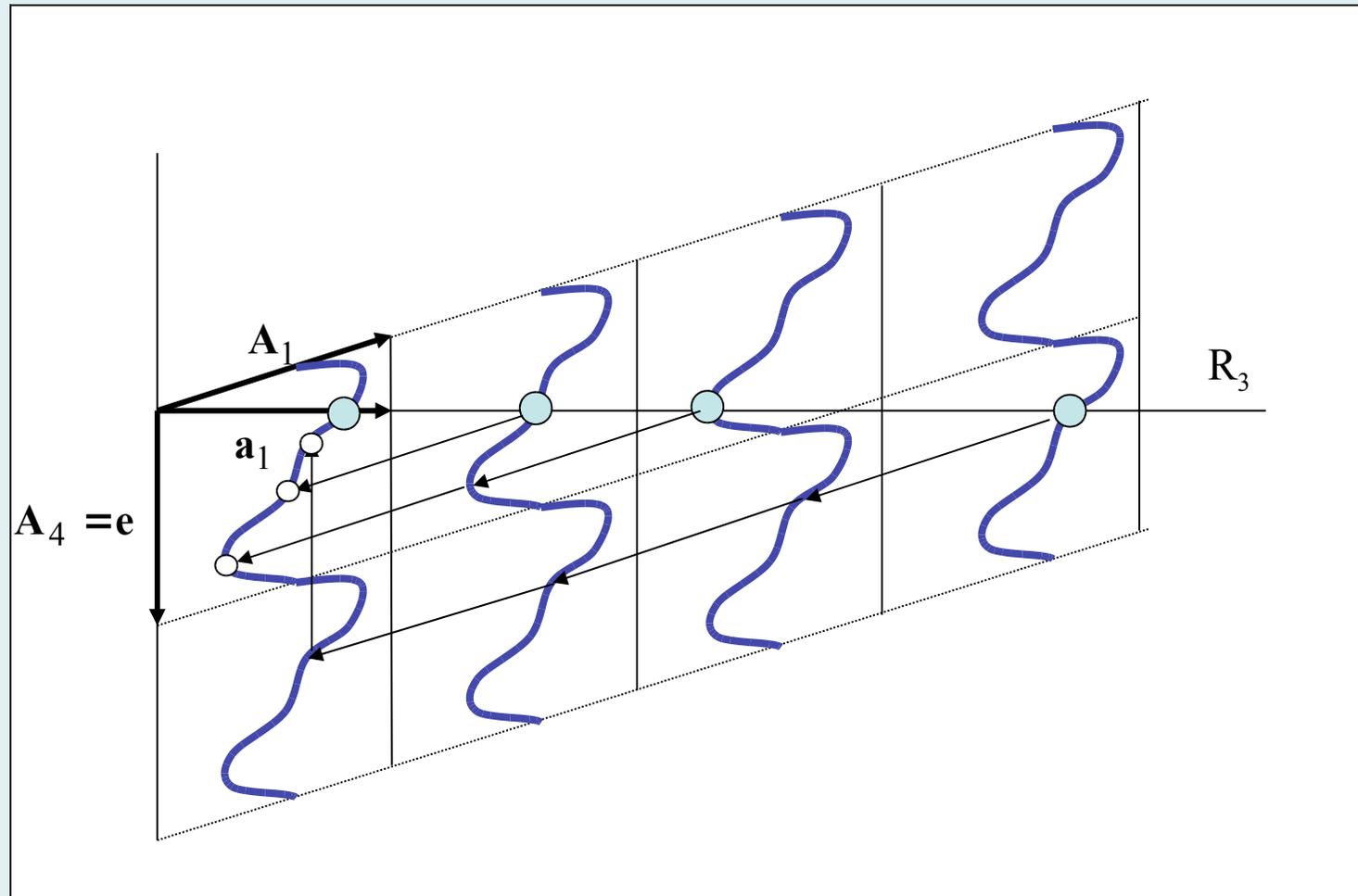
*Let us just discard **rhomboidal space groups**! Programs will be easier to write and less buggy. And that 1% of structures? We have already solved about a million structures, so who cares?*

A revolutionary proposal

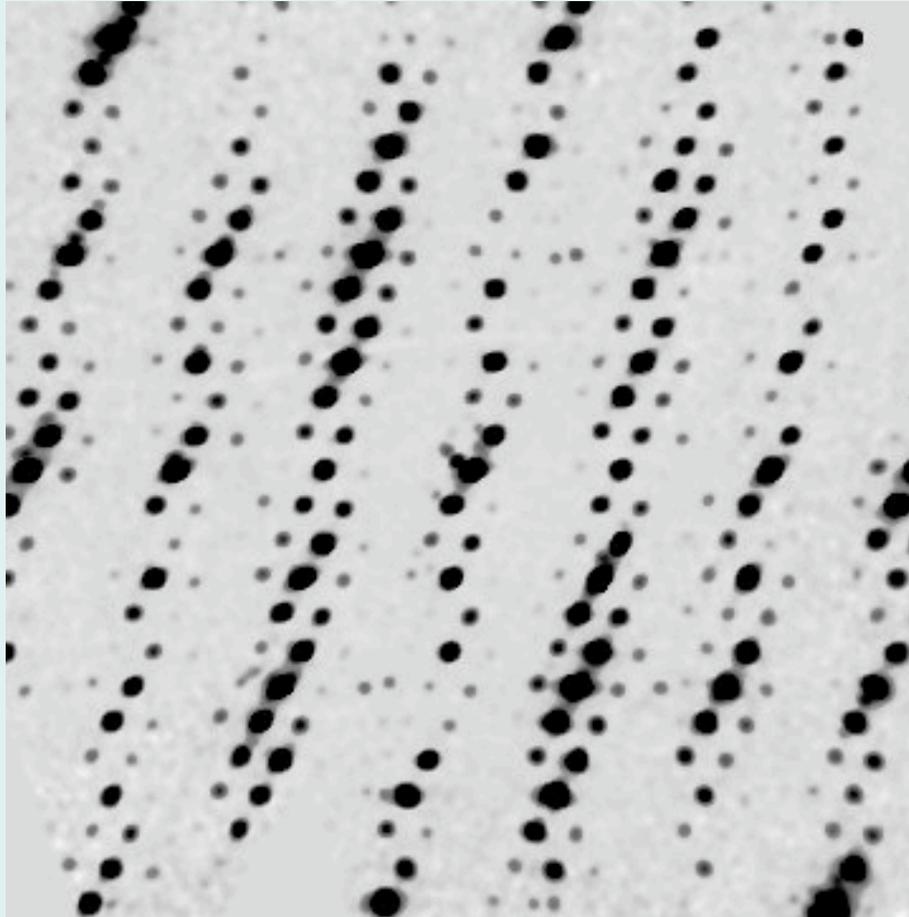
- **Incommensurate structures** are notoriously difficult to deal with.
- Their symmetry properties are different from other crystals, and require special handling
- They account only for about 1% of all structures (**wild guess here**)

*Let us just discard **incommensurate structures**! Programs will be easier to write and less buggy. And that 1% of structures? We have already solved about a million structures, so who cares?*

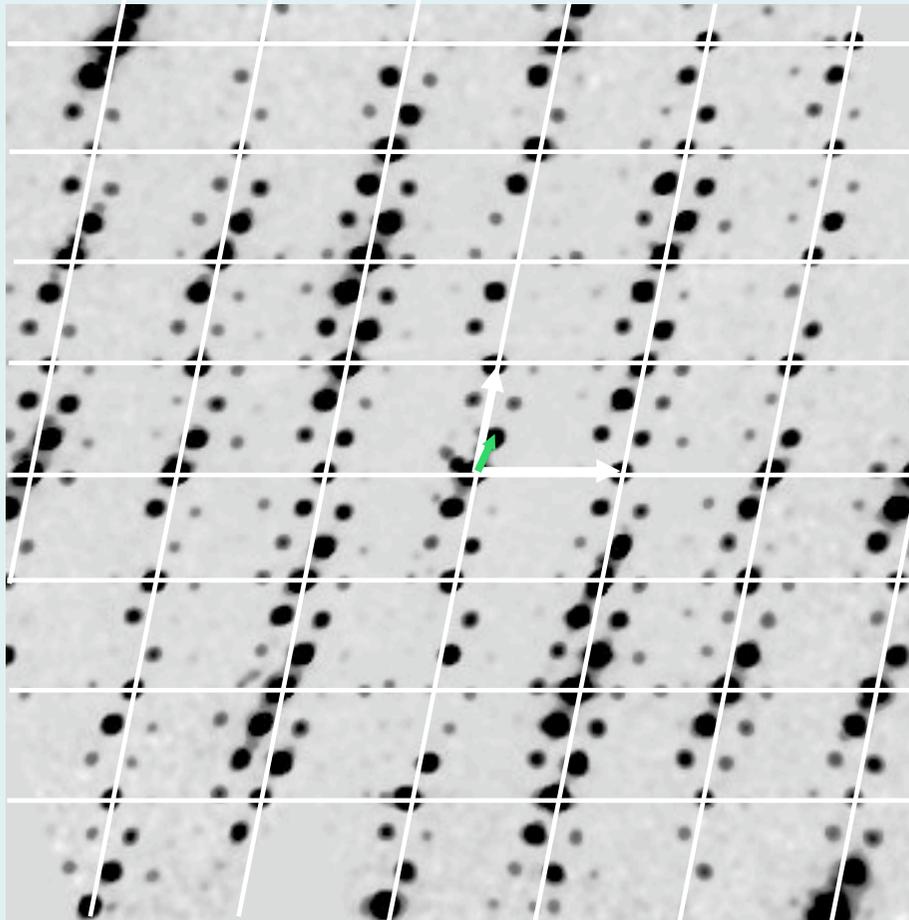
Superspace at a glance



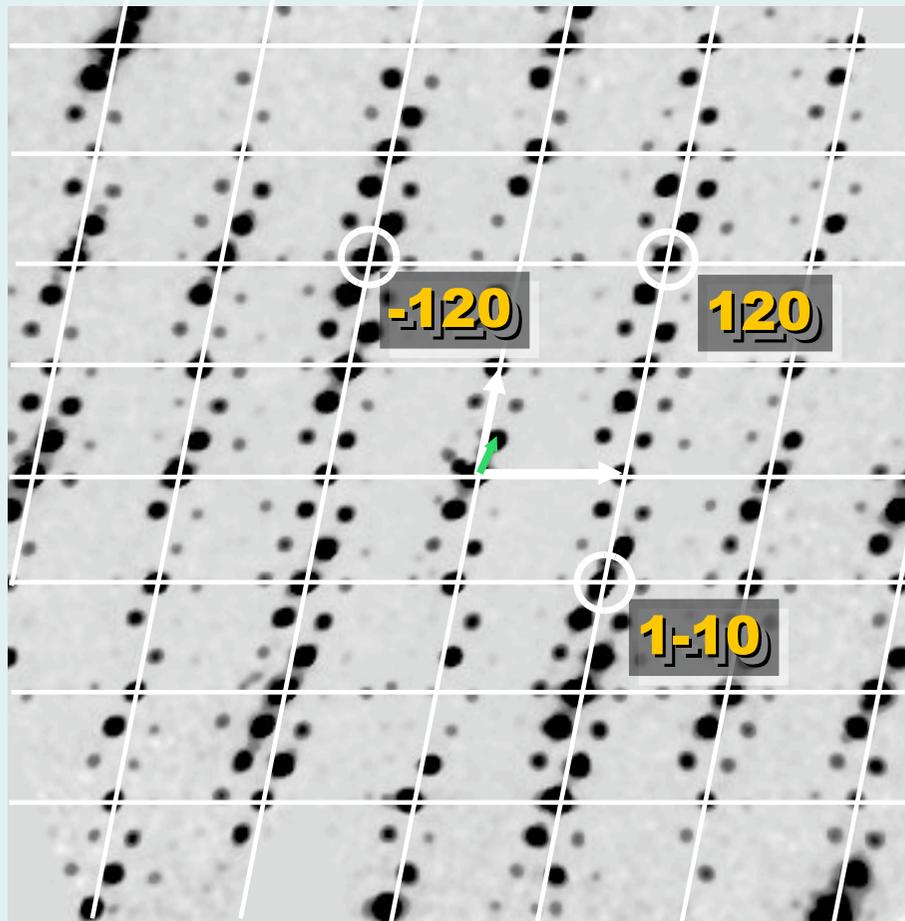
Reciprocal space



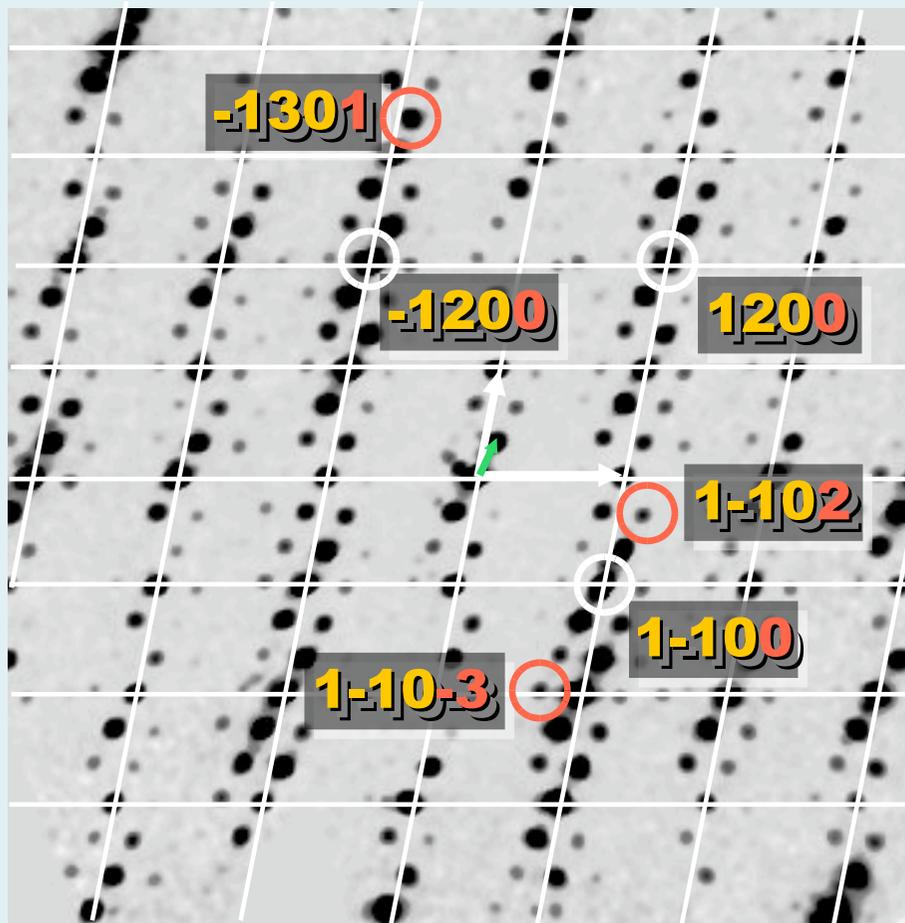
Reciprocal space



Reciprocal space



Reciprocal space



- When dealing with an incommensurately modulated structure we face four main challenges:
- Handling the diffraction pattern
- Handling the symmetry
- Computing the structure factor
- Computing structural properties (distances, angles...)

Common feature for all issues related to modulated structures: the use of superspace and work in more than 3 dimensions, but keeping in mind the relationship to 3D.

Diffraction pattern

3D

Properties:

- indices hkl
- diffraction vector
 $\mathbf{h} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$
- intensity $I(\mathbf{h})$
- structure factor $F(\mathbf{h})$
- d-spacing $d = 1/|\mathbf{h}|$

d_{\min} uniquely determines a set of reflections within certain resolution sphere

4D

Properties:

- indices $hklm$
- diffraction vector
 $\mathbf{h} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + m\mathbf{q}$
- intensity $I(\mathbf{h})$
- structure factor $F(\mathbf{h})$
- d-spacing $d = 1/|\mathbf{h}|$

d_{\min} and m_{\max} determine a set of reflections within certain resolution sphere

Symmetry

3D

3D symmetry operators:

$$S = (\mathbf{R}, \mathbf{t})$$

space group $G = \{S_i\}$

transformation of a vector:

$$\mathbf{r}' = \mathbf{R}\mathbf{r} + \mathbf{t}$$

transformation of an atom

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$$S = (\mathbf{R}, \mathbf{t})$$

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transformation of a vector:

$$\mathbf{r}' = \mathbf{R}\mathbf{r} + \mathbf{t}$$

transformation of an atom

$$\mathbf{r} = \mathbf{r}_0 + \mathbf{u}(x_4)$$

$$\mathbf{r}'_0 = \mathbf{R}_E \mathbf{r}_0 + \mathbf{t}_E$$

$$\mathbf{u}'(x_4) = \mathbf{R}_3 \mathbf{u}(R_{44}(x_4 - t_4))$$

General symmetry element: $S = \left(\begin{array}{c|c} \mathbf{R}_E & \mathbf{0} \\ \hline \mathbf{R}_M & \mathbf{R}_I \end{array} \right)$

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The only new information is the intrinsic part of the 4th component of the translation vector which, analogically to 3D symmetry, affects systematic absences of reflections. It expresses, how the modulation wave is shifted in the internal space. If \mathbf{t}_I is intrinsic, it can be determined from systematic absences.

Systematic absences

3D

- 1) Determine the invariant reflections of the rotation matrix from the relationship

$$\mathbf{h}_{\text{inv}} = \mathbf{h}_{\text{inv}} \mathbf{R}$$

- 2) The invariant reflections match the relationship

$$\mathbf{h} \cdot \mathbf{t} = n$$

Example: c-glide perp. to \mathbf{b} :

$$x_1, x_2, x_3 \rightarrow x_1, -x_2, \frac{1}{2} + x_3$$

$$\mathbf{h}_{\text{inv}} = (h, 0, l); \mathbf{h} \cdot \mathbf{t} = l/2 = n:$$

$$l = 2n$$

4D

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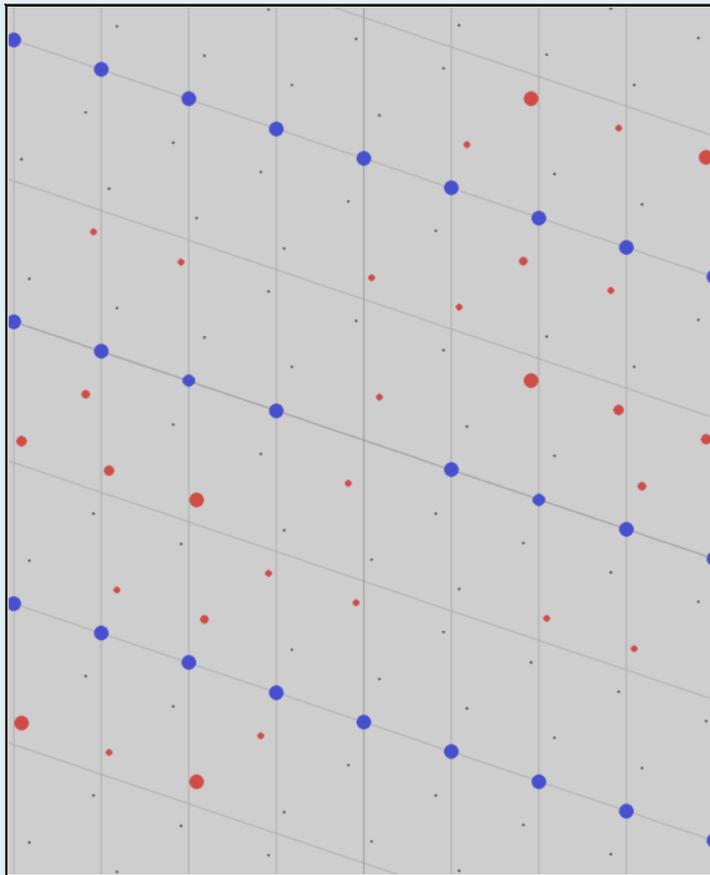
$$x_1, x_2, x_3, x_4 \rightarrow x_1, -x_2, \frac{1}{2} + x_3, \frac{1}{2} + x_4$$

$$\mathbf{h}_{\text{inv}} = (h, 0, l, m); \mathbf{h} \cdot \mathbf{t} = l/2 + m/2 = n:$$

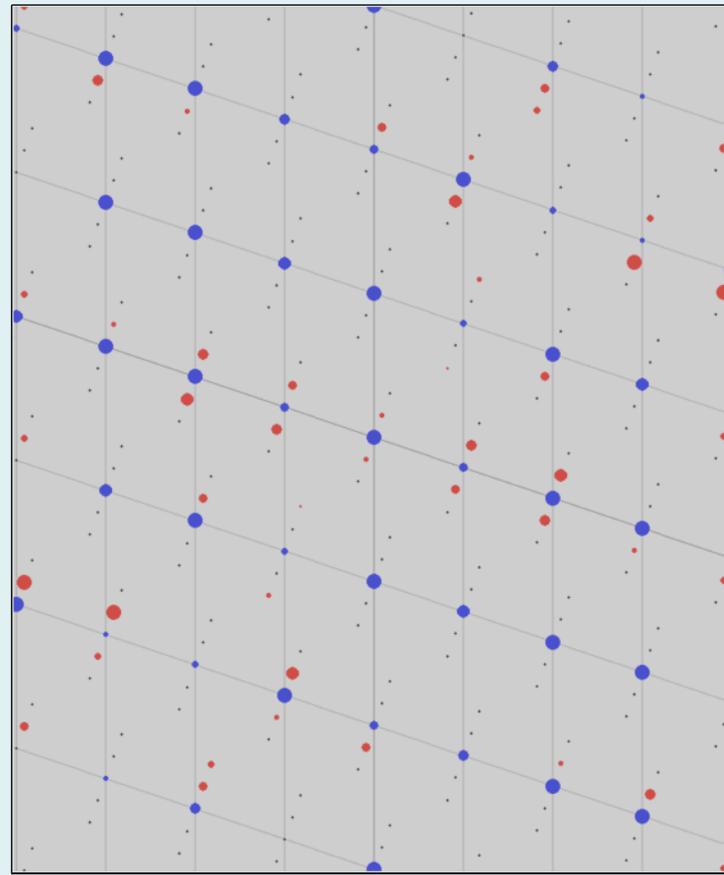
$$l + m = 2n$$

Systematic absences: $l+m=2n$

zero layer



first layer



Structure factor

3D

Basic formula:

$$F_{\mathbf{h}} = \int_V \rho(\mathbf{r}) \exp(2\pi i \mathbf{h} \cdot \mathbf{r}) dV$$

Integrating out the atomic densities:

$$F_{\mathbf{h}} = \sum_j f_j(h) \exp(2\pi i \mathbf{h} \cdot \mathbf{r}_j)$$

4D

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$$F_{\mathbf{h}} = \sum_j f_j(h) \exp(2\pi i \mathbf{h} \cdot \mathbf{r}_j) \times$$

$$\times \int_{x_4} \exp(2\pi i (u(x_4) + mx_4)) dx_4$$

Structure factor

$$F_{\mathbf{h}} = \sum_j f_j(h) \exp(2\pi i \mathbf{h} \cdot \mathbf{r}_j) \times \\ \times \int_{x_4} \exp(2\pi i (u(x_4) + mx_4)) dx_4$$

For simple modulations (straight lines, harmonic modulation functions) analytical formulae exist.

Various computing methods have been devised for fast calculation of the structure factor, but nowadays the „simple“ numerical integration (Gaussian quadrature) is used.

Poor man's solution: calculate superspace electron density on a regular grid, and get structure factors by FFT of the electron density

Some useful practical concepts

If you intend to make your program applicable to 3+n dimensions:

1) Do not fix the number of coordinates of your vectors to three.
Make all vectors n-dimensional instead.

This brings two main problems:

a) constructs like this one are impossible:

```
DO h=hmin,hmax
  DO k=kmin,kmax
    DO l=lmin,lmax
      some clever math here
    ENDDO
  ENDDO
ENDDO
```

Some useful practical concepts

If you intend to make your program applicable to 3+n dimensions:

1) Do not fix the number of coordinates of your vectors to three.

Make all vectors n-dimensional instead.

This brings two main problems:

a) instead you need:

setup starting and ending coordinates

DO

CALL GiveMeNextIndices(hkl, IsLast)

some clever math here

IF (IsLast) EXIT

ENDDO

Some useful practical concepts

If you intend to make your program applicable to 3+n dimensions:

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This brings two main problems:

b) multidimensional arrays (like electron density) must be stored in one-dimensional array. You have to write functions for transforming the index of the 1D array to the multidimensional indices and vice versa.

Some useful practical concepts

If you intend to make your program applicable to 3+n dimensions:

2) Avoid tables, especially symmetry tables. Use matrix algebra instead:

- it is more elegant
- does not suffer from the problem of non-standard settings
- tables for higher dimensions are very difficult to assemble
- algebraic approach is less prone to typing errors

Some useful practical concepts

If you intend to make your program applicable to 3+n dimensions:
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Symmetry operations compatible with the lattice and centering:

	Symmetry operation			agreement factor
n(0,1,0):	1/2+x1	-x2	1/2+x3	0.116
b(1,0,0):	-x1	1/2+x2	x3	0.184
2_1(0,0,1):	-x1	-x2	1/2+x3	0.237
2_1(1,0,0):	1/2+x1	-x2	-x3	33.107
-1:	-x1	-x2	-x3	33.207
m(0,0,1):	x1	x2	-x3	75.603
2_1(0,1,0):	-x1	1/2+x2	-x3	75.670
m(0,1,0):	x1	-x2	x3	82.962

Space group derived from the symmetry operations:

HM symbol: Pbn21
Hall symbol: P 2c -2ab
Fingerprint: 3300223}250qY2 (3/4,3/4,0)
Symmetry operations:

1:	x1	x2	x3
2_1(0,0,1):	-x1	-x2	1/2+x3
b(1,0,0):	1/2-x1	1/2+x2	x3
n(0,1,0):	1/2+x1	1/2-x2	1/2+x3

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Useful exercise

You may try to practice some of the superspace concepts by writing the following program:

Given a superspace group (as a list of one-line representations of **R** and **t**), produce a list of all systematically absent reflections within a given resolution sphere and given maximal satellite index.