Data items revised in these categories are as follows:

(*a*) AUDIT
`_audit_block_code`
(*b*) AUDIT_LINK
`_audit_link_block_code`

The core dictionary definitions of these items are revised in order to formalize the relationships between multiple data blocks representing reference and modulated structures. Guidance is provided in the msCIF dictionary on how to label data blocks in a way that makes their mutual relationships clear.

3.4.4. Use of the msCIF dictionary

In this section, some of the capabilities of the dictionary will be demonstrated using simple examples. More detailed examples can be found at http://www.iucr.org/iucr-top/cif/ms and on the CD-ROM accompanying this volume.

3.4.4.1. Description of reciprocal space

Modulated and composite structures need more than three reciprocal vectors in order to index the whole set of reflections with integer numbers. Hence a diffraction vector is written as

$$\mathbf{H} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + m_1\mathbf{q}_1 + \ldots + m_d\mathbf{q}_d, \qquad (3.4.4.1)$$

where the notation has been chosen according to the core CIF dictionary. In the case of a modulated structure, $\mathbf{a}^*$, $\mathbf{b}^*$ and $\mathbf{c}^*$ are the reciprocal vectors of the reference structure (and therefore h, k and l index the main reflections). $\mathbf{q}_1, \ldots, \mathbf{q}_d$ are the modulation wave vectors. They are three-dimensional vectors with some irrational component (if the modulated structure is incommensurate) in the lattice spanned by $\mathbf{a}^*$, $\mathbf{b}^*$ and $\mathbf{c}^*$. d is the dimension of the modulation. In the case of composite structures, the diffraction pattern can be indexed using $3 + d$ (arbitrarily selected) vectors $\mathbf{a}_k^*$ ($k = 1, \ldots, 3+d$). $\mathbf{a}_1^*$ ($\equiv \mathbf{a}^*$), $\mathbf{a}_2^*$ ($\equiv \mathbf{b}^*$) and $\mathbf{a}_3^*$ ($\equiv \mathbf{c}^*$) normally span the reciprocal lattice of the main reflections of one of the substructures (notice that this is only one particular, but highly intuitive, choice). The remaining d vectors with $k = 4, \ldots, d$ are the wave vectors of the modulation [$\mathbf{q}_1, \ldots, \mathbf{q}_d$ in equation (3.4.4.1)].

In a composite structure, the $(3 + d)$-dimensional reciprocal basis of the subsystem ν is determined by a $(3 + d) \times (3 + d)$ matrix W^ν [see van Smaalen (1995) and references therein]:

$$\mathbf{a}_i^{*\nu} = \sum_{k=1}^{3+d} W_{ik}^\nu \mathbf{a}_k^*, \quad i = 1, \ldots, 3 + d, \qquad (3.4.4.2)$$

where the subscripts $i = 1$, 2 and 3 label the reciprocal vectors $\mathbf{a}^{*\nu}$, $\mathbf{b}^{*\nu}$ and $\mathbf{c}^{*\nu}$, and $i = 4, \ldots, d$ label the wave vectors of the modulation expressed as linear combinations of $\mathbf{a}^{*\nu}$, $\mathbf{b}^{*\nu}$ and $\mathbf{c}^{*\nu}$.

The simplest case corresponds to a one-dimensional ($d = 1$) modulated structure. Consider for example the incommensurate phase of K_2SeO_4. The wave vector of the modulation can be chosen to be $\mathbf{q}_1 = \alpha\mathbf{a}^*$. Relevant information about the diffraction pattern of this compound is expressed using both the core CIF and msCIF dictionaries as shown in Example 3.4.4.1.

A more complicated example is the composite structure $(LaS)_{1.14}NbS_2$. The two mutually incommensurate subsystems (along the a axis) are (van Smaalen, 1991) NbS_2 ($\nu = 1$) and LaS ($\nu = 2$). The reciprocal basis can be chosen to be $\mathbf{a}_1^* = \mathbf{a}^{*1}$, $\mathbf{a}_2^* = \mathbf{b}^{*1}$, $\mathbf{a}_3^* = \mathbf{c}^{*1}$ and $\mathbf{a}_4^* = \mathbf{a}^{*2}$. For this particular choice, the two W matrices [see equation (3.4.4.2)] are

Example 3.4.4.1. *msCIF description of the diffraction pattern of a one-dimensional modulated structure.*

```
_exptl_crystal_type_of_structure         'mod'
_cell_reciprocal_basis_description
; a*,b*,c* (reciprocal basis spanning the lattice of
  main reflections), q modulation wave vector.
;

_diffrn_symmetry_description
; The whole diffraction pattern shows orthorhombic
  symmetry. The following extinction rules were
  detected:
     0kl0    k+l=odd
     h0lm    h+m=odd
     hk0m    m=odd
     h00m    h,m=odd
  Superspace group: P:Pnam:-1ss
;

_diffrn_reflns_satellite_order_max            1

_diffrn_reflns_theta_max                  40.14
_diffrn_reflns_theta_min                   3.32
_diffrn_reflns_limit_h_max                    8
_diffrn_reflns_limit_k_max                   18
_diffrn_reflns_limit_l_max                   10
_diffrn_reflns_limit_index_m_1_max            1
_diffrn_reflns_limit_h_min                    0
_diffrn_reflns_limit_k_min                    0
_diffrn_reflns_limit_l_min                    0
_diffrn_reflns_limit_index_m_1_min           -1

# Modulation wave vector
  loop_
     _cell_wave_vector_seq_id
     _cell_wave_vector_x
         1        0.318(5)
```

$$W^1 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}, \quad W^2 = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix}.$$

This information is transcribed to CIF format as shown in Example 3.4.4.2. (Note that the default values for the wave vector components and the elements of W are 0.)

3.4.4.2. Description of symmetry

The symmetry of a modulated or composite structure is described by a superspace group which leaves the $(3 + d)$-dimensional embedding of the structure invariant. Superspace is built of two orthogonal subspaces and both of them are kept invariant separately by the superspace symmetry operations. (In reciprocal space this means that, for these structures, main reflections and satellite reflections are never transformed into one another by superspace symmetry operations.) Consequently, superspace groups are not general $(3 + d)$-dimensional space groups. The standard notation for superspace groups only covers the one-dimensional superspace groups, which are listed in Janssen *et al.* (2004). As a consequence, msCIFs must include a list of all the symmetry operations in an (x, y, z) format (using as symbols $x_1 \ldots x_{3+d}$) similar to that used in the core CIF dictionary. Superspace-group names for one-dimensional structures can be expressed either according to Janssen *et al.* (2004) or according to the original notation of de Wolff *et al.* (1981). Alternative names or higher-dimensional superspace groups can also be included, but not parsed.

Example 3.4.4.2. *Representation of two mutually incommensurate subsystems.*

```
_exptl_crystal_type_of_structure        'comp'
_cell_subsystems_number                  2
_cell_modulation_dimension               1

_cell_reciprocal_basis_description
; a1*,b1*,c1* (reciprocal basis spanning the
  reciprocal basis of the first subsystem),
  a2* reciprocal axis corresponding to the
  second subsystem.
;

loop_
  _cell_subsystem_code
  _cell_subsystem_description
  _cell_subsystem_matrix_W_1_1
  _cell_subsystem_matrix_W_1_4
  _cell_subsystem_matrix_W_2_2
  _cell_subsystem_matrix_W_3_3
  _cell_subsystem_matrix_W_4_1
  _cell_subsystem_matrix_W_4_4
     NbS2  '1st subsystem'  1 0 1 1 0 1
     LaS   '2nd subsystem'  0 1 1 1 1 0

_diffrn_symmetry_description
; The whole diffraction pattern shows orthorhombic
  symmetry. The following extinction rules were
  detected:
     hklm   h+k+m=odd
     hklm   h+l=odd
     hklm   k+l+m=odd
     hk0m   h+k=odd
     hk0m   m=odd
  Extinction rules are compatible with the superspace
  groups:
     P:Fmmm:-11s(\a,0,0)
     P:Fm2m:-1-1s(\a,0,0)
;
```

Example 3.4.4.3. *Symmetry description of a superspace group.*

```
_space_group_ssg_name_WJJ   'P:P n a m:-1 s s'
_space_group_ssg_name_IT    'P n m a (\a 0 0) 0 s s'

loop_
     _space_group_symop_ssg_id
     _space_group_symop_ssg_operation_algebraic
     1   x1,x2,x3,x4
     2   1/2+x1,1/2-x2,1/2-x3,x4
     3   1/2-x1,1/2+x2,-x3,1/2-x4
     4   -x1,-x2,1/2+x3,1/2-x4
     5   -x1,-x2,-x3,-x4
     6   1/2-x1,1/2+x2,1/2+x3,-x4
     7   1/2+x1,1/2-x2,x3,1/2+x4
     8   x1,x2,1/2-x3,1/2+x4
```

In the particular case of K_2SeO_4, the superspace group is $P^{Pnma}_{\bar{1}\,s\,s}$ (de Wolff *et al.*, 1981) or $Pnma(\alpha 00)0ss$ (Janssen *et al.*, 2004). This information would appear in a CIF as shown in Example 3.4.4.3.

Example 3.4.4.4. *Atomic displacements as translations and rigid rotations.*

```
loop_
  _atom_site_description
  _atom_site_label
  _atom_site_occupancy
  _atom_site_fract_x
  _atom_site_fract_y
  _atom_site_fract_z
; SeO4 is a tetrahedral group formed by the atoms
  Se, O1, O2, O3 and O1p. O1p is related to O1 by the
  mirror plane perpendicular to the c axis. The
  coordinates given by _atom_site_fract_ correspond
  to the centre of mass.
;
     SeO4 1.0  0.22346    0.41868    0.250000
  .  Se   1.0  0.22216(4) 0.41861(3) 0.250000
  .  K1   1.0  0.1670(1)  0.08069(7) 0.250000
  .  K2   1.0 -0.0013(1)  0.70766(4) 0.250000
  .  O1   1.0  0.2890(3)  0.3413(2)  0.0277(3)
  .  O2   1.0  0.3130(4)  0.5621(2)  0.250000
  .  O3   1.0  0.0092(4)  0.4304(3)  0.250000

_refine_ls_mod_func_description
; Displacive modulation. Fourier series. Modulation
  of SeO4 group described in terms of rigid
  translations and rotations.
;

loop_
  _atom_site_Fourier_wave_vector_seq_id
  _atom_site_Fourier_wave_vector_x
  _atom_site_Fourier_wave_vector_description
     1   0.318(5)   'First harmonic'

loop_
  _atom_site_displace_Fourier_id
  _atom_site_displace_Fourier_atom_site_label
  _atom_site_displace_Fourier_axis
  _atom_site_displace_Fourier_wave_vector_seq_id
     K1_z_1   K1     z   1
     K2_z_1   K2     z   1
     SeO_z_1  SeO4   z   1

loop_
  _atom_site_displace_Fourier_param_id
  _atom_site_displace_Fourier_param_cos
  _atom_site_displace_Fourier_param_sin
     K1_z_1    0.0080(4)  -0.0106(5)
     K2_z_1    0.0159(4)   0.0071(6)
     SeO_z_1  -0.0089(2)  -0.0058(2)

loop_
  _atom_site_rot_Fourier_id
  _atom_site_rot_Fourier_atom_site_label
  _atom_site_rot_Fourier_axis
  _atom_site_rot_Fourier_wave_vector_seq_id
     SeO_x_1   SeO4   x   1
     SeO_y_1   SeO4   y   1

loop_
  _atom_site_rot_Fourier_param_id
  _atom_site_rot_Fourier_param_cos
  _atom_site_rot_Fourier_param_sin
     SeO_x_1  -4.2(1)   0.91(3)
     SeO_y_1   4.3(1)   0.
```

3.4.4.3. Description of the structure

A modulated structure is described by a reference periodic structure and the atomic modulation functions. Such functions are periodic and are normally expanded as Fourier series. The modulated parameters may apply to the atom positions (displacive modulation), the site occupancies (occupational modulation) and/or the temperature factors. In composite structures, each substructure is referred to the crystallographic basis defined by the W matrices [see equation (3.4.4.2)]. The simplest case corresponds to a one-dimensional displacive modulated structure. In this case, the atomic modulation functions are given by

$$u^{\mu}_{\alpha} = \sum_{n=1}^{\infty} U^{\mu}_{n\alpha} \cos\left(2\pi n\mathbf{q}\cdot\mathbf{r} + \varphi^{\mu}_{n\alpha}\right), \qquad (3.4.4.3)$$

where $(U^{\mu}_{n\alpha}, \varphi^{\mu}_{n\alpha})$ is the complex amplitude of each Fourier term; μ labels the atoms; $\alpha = x, y, z$; $\mathbf{r}$ is the average atom position; and $n\mathbf{q}$ represents the successive harmonics of the modulation. At present, displacive modulations along axes other than a, b and c can be calculated with the restriction stated in Section 3.4.2.