should be noted that the diffraction pattern of a modulated crystal is obtained by a projection of the Fourier transform of the (3 + 1)-dimensional periodic structure. Fig. 2.5.3.18(*b*) is assumed to be the Fourier transform of Fig. 2.5.3.17(*b*). Incommensurate reflections are obtained by a projection of the reciprocal-lattice points onto $\mathbf{R}_3^*$.

The displacive modulation is expressed by the atom displacement u_i^μ with x_4. The structure factor $F(h_1h_2h_3h_4)$ for the (3 + 1)-dimensional crystal with a displacive modulation is given by de Wolff (1974, 1977) as follows:

$$F(h_1h_2h_3h_4) = \sum_{\mu=1}^{N} f_\mu \exp[2\pi i(h_1\bar{x}_1^\mu + h_2\bar{x}_2^\mu + h_3\bar{x}_3^\mu)] \times \int_0^1 \exp\left\{2\pi i\left[\sum_{i=1}^{3}(h_i + h_4k_i)u_i^\mu + h_4\bar{x}_4^\mu\right]\right\} \mathrm{d}\bar{x}_4^\mu, \tag{2.5.3.6}$$

where

$$\bar{x}_4^\mu = (\bar{x}_1^\mu + n_1)k_1 + (\bar{x}_2^\mu + n_2)k_2 + (\bar{x}_3^\mu + n_3)k_3.$$

f_μ and $\bar{x}_i^\mu (i = 1\text{–}3)$ are, respectively, the atom form factor and the ith component of the position of the μth atom in the unit cell of the average structure. The symbol u_i^μ is the ith component of the displacement of the μth atom. Since the atom in the (3 + 1)-dimensional space is continuous along $\mathbf{a}_4$ and discrete along $\mathbf{R}_3$, the structure factor is expressed by summation in $\mathbf{R}_3$ and integration along $\mathbf{a}_4$ as seen in equation (2.5.3.6). The integration implies that the sum for the atoms with displacements is taken over the infinite number of unit cells of the average structure. That is, equation (2.5.3.6) is the structure factor for a unit cell with the lattice parameter of an infinite length in $\mathbf{R}_3$ along the direction of the modulation wavevector $\mathbf{k}$.

CBED patterns are obtained from a finite area of a specimen crystal. For the symmetry analysis of CBED patterns obtained from modulated structures, the effect of the finite size was considered by Terauchi & Tanaka (1993). The integration over a unit-cell length along $\mathbf{a}_4$ in equation (2.5.3.6) is rewritten in the following way with the summation over a finite number of three-dimensional sections of the atom strings:

$$F'(h_1h_2h_3h_4) = \sum_{\mu=1}^{N} f_\mu \exp[2\pi i(h_1\bar{x}_1^\mu + h_2\bar{x}_2^\mu + h_3\bar{x}_3^\mu)] \times \sum_{n_1}\sum_{n_2}\sum_{n_3} \exp\left\{2\pi i\left[\sum_{i=1}^{3}(h_i + h_4k_i)u_i^\mu + h_4\bar{x}_4^\mu\right]\right\}, \tag{2.5.3.7}$$

where $N_1 < n_1 \le N_1'$, $N_2 < n_2 \le N_2'$ and $N_3 < n_3 \le N_3'$, $N' = (N_1' - N_1)(N_2' - N_2)(N_3' - N_3)$ being the number of unit cells of the average structure included in a specimen volume from which CBED patterns are taken.

The substitutional modulation arises from a periodic variation of the site-occupation probability of the atoms. This modulation is expressed by a modulation of the atom form factor f_μ with x_4. The structure factor $F'(h_1h_2h_3h_4)$ for a finite-size crystal is written as

$$F'(h_1h_2h_3h_4) = \sum_{\mu=1}^{N} \exp[2\pi i\,(h_1x_1^\mu + h_2x_2^\mu + h_3x_3^\mu)] \times \sum_{n_1}\sum_{n_2}\sum_{n_3} f_\mu \exp(2\pi i h_4 x_4^\mu), \tag{2.5.3.8}$$

where $x_4^\mu = \sum_i (x_i^\mu + n_i)k_i$.

2.5.3.4.2. Point-group determination

The symmetries of the CBED patterns can be determined by examination of the symmetries of the structure factor $F'(h_1h_2h_3h_4)$ in equations (2.5.3.7) or (2.5.3.8). We consider a displacive modulated structure, which has a modulation wavevector $\mathbf{k} = k_3\mathbf{c}^*$ and belongs to (3 + 1)-dimensional space group $P^{P2/m}_{1\ \bar{1}}$. This space-group symbol implies the following.

(1) The modulation wavevector $\mathbf{k}$ exists inside the first Brillouin zone of the average structure (P).

(2) The average structure belongs to space group $P2/m$, the twofold rotation axis being parallel to the c axis.

(3) The symmetry subsymbol 1, which is written beneath symmetry symbol 2, indicates that the modulation wavevector $\mathbf{k}$ is transformed into itself by symmetry operation 2 of the average structure. The symmetry subsymbol beneath symmetry symbol m indicates that the wavevector $\mathbf{k}$ is transformed into $-\mathbf{k}$ by symmetry operation m. The modulated structure has a twofold rotation axis, which is common to the average structure, but does not have mirror symmetry, which is possessed by the average structure.

For the twofold rotation axis (symbol 2) of this space group, the structure factor $F'(h_1h_2h_3h_4)$ is written as

$$\begin{aligned} F'(h_1h_2h_3h_4) &= \sum_{\mu=1}^{N} f_\mu \exp[2\pi i(h_1\bar{x}_1^\mu + h_2\bar{x}_2^\mu + h_3\bar{x}_3^\mu)] \\ &\quad \times \sum_{n_3} \exp\{2\pi i[h_1u_1^\mu + h_2u_2^\mu + (h_3 + h_4k_3)u_3^\mu + h_4\bar{x}_4^\mu]\} \\ &\quad + \sum_{\mu=1}^{N} f_\mu \exp[2\pi i(-h_1\bar{x}_1^\mu - h_2\bar{x}_2^\mu + h_3\bar{x}_3^\mu)] \\ &\quad \times \sum_{n_3} \exp\{2\pi i[-h_1u_1^\mu - h_2u_2^\mu + (h_3 + h_4k_3)u_3^\mu + h_4\bar{x}_4^\mu]\}, \end{aligned} \tag{2.5.3.9}$$

where $x_4^\mu = (x_3^\mu + n_3)k_3$. It is found from equation (2.5.3.9) that two structure factors $F'(h_1h_2h_3h_4)$ and $F'(\bar{h}_1\bar{h}_2h_3h_4)$ are the same when reflections $h_1h_2h_3h_4$ and $\bar{h}_1\bar{h}_2h_3h_4$ are equivalent with respect to the twofold rotation axis of the average structure. Thus, not only fundamental reflections ($h_4 = 0$) from the average structure but also the satellite reflections ($h_4 \neq 0$) from the incommensurate structure show twofold rotation symmetry about the c^* axis.

For the mirror plane (symbol m), the structure factor is written in a similar manner to the case of the twofold rotation axis. It is found that $F'(h_1h_2h_3h_4)$ is not equal to $F'(h_1h_2\bar{h}_3\bar{h}_4)$ for the incommensurate reflections $h_4 \neq 0$. Hence, the incommensurate reflections do not show mirror symmetry with respect to the mirror plane of the average structure. For the fundamental reflections ($h_4 = 0$), $F'(h_1h_2h_3h_4)$ is equal to $F'(h_1h_2\bar{h}_3\bar{h}_4)$, indicating the existence of mirror symmetry. It should be noted that the mirror symmetry can be destroyed by the dynamical diffraction effect between the fundamental and incommensurate reflections. In most modulated structures, however, the amplitude of the modulation wave u_i^μ is not so large as to destroy the symmetry of the fundamental reflections. Thus, the fundamental

Table 2.5.3.13. *Wavevectors, point- and space-group symbols and CBED symmetries of one-dimensionally modulated crystals*

Wavevector transformation	Point-group symbol	Symmetry of incommensurate reflection	Space-group symbol	Dynamical extinction lines
$\mathbf{k} \rightarrow \mathbf{k}$	1	Same symmetry as average structure	1, s (1/2), t ($\pm$1/3), q ($\pm$1/4), h ($\pm$1/6)	Yes for s, q and h
$\mathbf{k} \rightarrow -\mathbf{k}$	$\bar{1}$	No symmetry	$\bar{1}$	No

reflections ought to show the symmetry of the average structure, while the incommensurate reflections lose the symmetry.

The problem of the finite size of the illuminated area is discussed using equations (2.5.3.7) and (2.5.3.8) in a paper by Terauchi & Tanaka (1993) and in the book by Tanaka *et al.* (1994, pp. 156–205). The results are as follows: Even if the size and position of an illuminated specimen area are changed, the intensity distribution in a CBED pattern changes but the symmetry of the pattern does not. To obtain the symmetries of incommensurate crystals, it is not necessary to take CBED patterns from an area whose diameter is larger than the period of the modulated structure. The symmetries of the modulated structure can appear when more than one unit cell of the average structure is illuminated for displacive modulations. For substitutional modulations, a specimen volume that produces the average atom form factor is needed, namely a volume of about 1 nm diameter area and 50 nm thick.

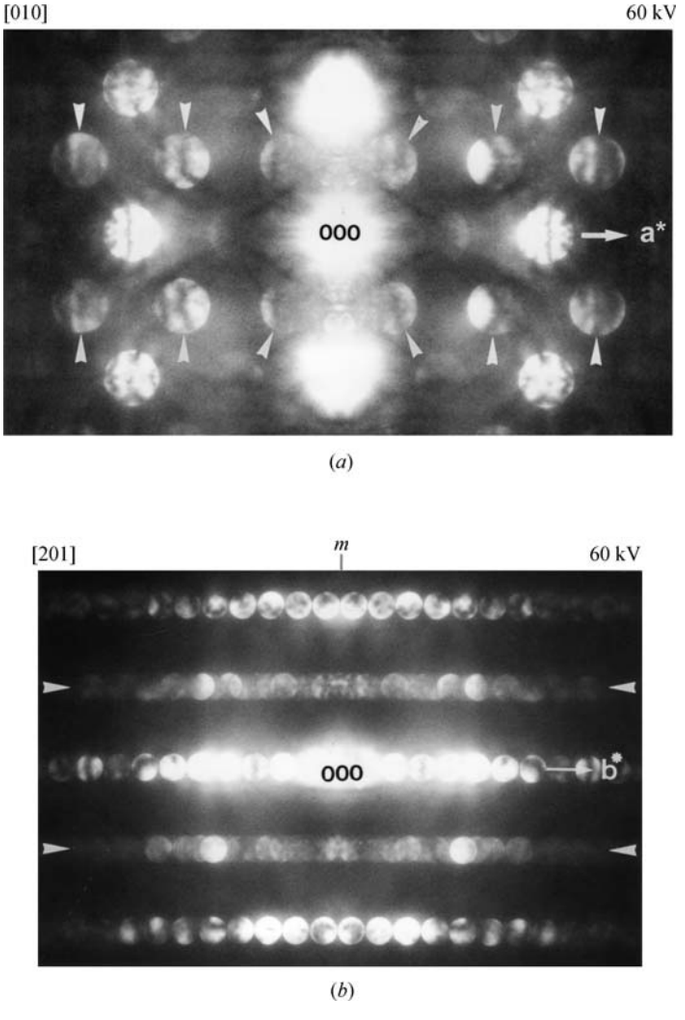

Fig. 2.5.3.19. CBED patterns of the incommensurate phase of $Sr_2Nb_2O_7$ taken at 60 kV. (*a*) [010] incidence: fundamental reflections show a mirror symmetry perpendicular to the a^* axis but incommensurate reflections do not [symmetry ($^m_1$)]. (*b*) [201] incidence: incommensurate reflections show mirror symmetry perpendicular to the b^* axis [symmetry ($^m_1$)]. The wave number vector of the modulation is $\mathbf{k} = (\frac{1}{2} - \delta)\mathbf{a}^*$.

Table 2.5.3.13 shows the point-group symmetries (third column) of the incommensurate reflections for the two point-group subsymbols. For symmetry subsymbol 1, both the fundamental and incommensurate reflections show the symmetries of the average structure. For symmetry subsymbol $\bar{1}$, the fundamental reflections show the symmetries of the average structure but the incommensurate reflections do not have any symmetry. These facts imply that the symmetries of the incommensurate reflections are determined by the point group of the average structure and the modulation wavevector **k**. In other words, observation of the symmetries of the incommensurate reflections is not necessary for the determination of the point groups, although it can ascertain the point groups of the modulated crystals.

An example of point-group determination is shown for the incommensurate phase of $Sr_2Nb_2O_7$. Many materials of the $A_2B_2O_7$ family undergo phase transformations from space group $Cmcm$ to $Cmc2_1$ and further to $P2_1$ with decreasing temperature. An incommensurate phase appears between the $Cmc2_1$ phase and the $P2_1$ phase. $Sr_2Nb_2O_7$ transforms at 488 K from the $Cmc2_1$ phase into the incommensurate phase with a modulation wavevector $\mathbf{k} = (\frac{1}{2} - \delta)\mathbf{a}^*$ (δ = 0.009–0.023) but does not transform into the $P2_1$ phase. The space group of $Sr_2Nb_2O_7$ was reported as $P^{C\,mc2_1}_{\bar{1}s\bar{1}}$ (Yamamoto, 1988). (Since the space-group notation $Cmc2_1$ is broadly accepted, the direction of the modulation is taken as the a axis.) The point group of the phase is $^{mm2}_{\bar{1}\,\bar{1}\,1}$. The modulation wavevector **k** is transformed to $-\mathbf{k}$ by the mirror symmetry operation perpendicular to the a axis ($^m_1$) and by the twofold rotation symmetry operation about the c axis ($^2_1$). The wavevector is transformed into itself by the mirror symmetry operation perpendicular to the b axis ($^m_1$).

Fig. 2.5.3.19(*a*) shows a CBED pattern of the incommensurate phase of $Sr_2Nb_2O_7$ taken with the [010] incidence at an accelerating voltage of 60 kV. The reflections indicated by arrowheads are the incommensurate reflections. Other reflections are the fundamental reflections. Since the pattern is produced by the interaction of the reflections in the zeroth-order Laue zone, symmetry operations ($^m_1$) and ($^2_1$) act the same. These symmetries are confirmed by the fact that the fundamental reflections show mirror symmetry perpendicular to the a^* axis (twofold rotation symmetry about the c^* axis) but the incommensurate reflections do not. Fig. 2.5.3.19(*b*) shows a CBED pattern of the incommensurate phase of $Sr_2Nb_2O_7$ taken with the [201] incidence at 60 kV. The reflections in the two rows indicated by arrowheads are the incommensurate reflections and the others are the fundamental reflections. Symmetry symbol ($^m_1$) implies that both the fundamental and incommensurate reflections display mirror symmetry perpendicular to the b^* axis. Fig. 2.5.3.19(*b*) exactly exhibits the symmetry.

2.5.3.4.3. Space-group determination

Table 2.5.3.13 shows the space-group symbols (fourth column) of the modulated crystals. When a glide (screw) component τ_4 between the modulation waves of two atom rows is 0, 1/2, $\pm$1/3, $\pm$1/4 or $\pm$1/6, symbol 1, s, t, q or h is given, respectively (de Wolff *et al.*, 1981). Such glide components are allowed for point-group symmetry 1 but are not for point-group symmetry $\bar{1}$. Dynamical