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The incommensurately modulated non-stoichiometric ytterbium sulphide phase $Yb_{3-\delta}S_4$

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Abstract. The extinction conditions associated with the observed incommensurate satellite reflections of the low (i.e. $\lesssim 1400$ °C) specimen preparation temperature $Yb_{3-\delta}S_4$ phase are used to provide a crystallographic description of this modulated structure. The superspace group is found to be P^{Pnma}_{11s} if the primary modulation wave-vector is chosen to fall inside the first Brillouin zone of the average structure.

1. Introduction

The Yb_3S_4 structure type (see figure 1) has been shown to be closely related to the warwickite type by single crystal x-ray structure analysis. It may be described as NaCl-type (B1) ribbons, $4 \times 1 \times \infty$ octahedra in extent, twinned by a glide-reflection operation (Hyde *et al* 1980) with strings of Yb-centred S_6 trigonal prisms filling the gaps between the octahedral ribbons. Early x-ray diffraction, density and magnetic susceptibility studies (Domange *et al* 1958, Flahaut *et al* 1960; Flahaut *et al* 1961) suggested that this phase had a continuous range of homogeneous solid solution from approximately Yb_3S_4 towards, but stopping short of, Yb_2S_3 ($=Yb_{2.66}S_4$): $Yb_3S_4 \rightarrow Yb_{2.74}S_4$. The magnetic susceptibility measurements showed the stoichiometric Yb_3S_4 compound to be $Yb^{2+}Yb_2^{3+}S_4^{2-}$, while the various Yb–S bond lengths obtained from the x-ray diffraction study indicated (and bond length/bond strength calculations unequivocally confirm) that Yb^{2+} is located in the trigonal prism sites and Yb^{3+} in the octahedral sites. Furthermore, the single crystal x-ray structure analysis showed that the stoichiometric range was accommodated by a proportion of the trigonal prism cation sites (up to about a quarter at $Yb_{2.74}S_4$) being emptied in association with oxidation of some of the remaining Yb^{2+} in these sites: $3Yb^{2+} \rightarrow 2Yb^{3+} + \square$, and apparently in a random manner (Chevalier *et al* 1967). The average structure of $Yb_{2.90}S_4$ determined by Chevalier *et al* (1967) had space group *Pnma*, with lattice parameters $a = 12.71$ Å, $b = 3.60$ Å, $c = 12.88$ Å and contained four formula units.

The recent discovery that these phases were incommensurately, and one-dimensionally, modulated along the b^* axis with a composition-dependent primary modulation wavevector (Plug 1980, Otero-Diaz and Hyde 1983) is thus most naturally interpreted

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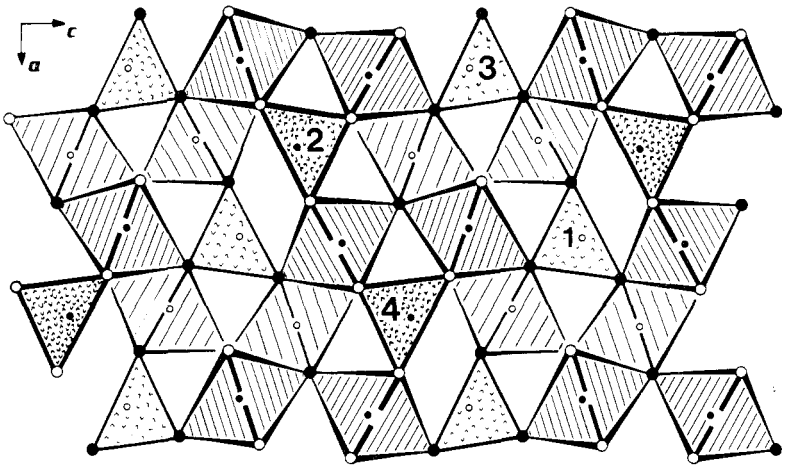

Figure 1. The structure of Yb_3S_4 projected on (010). Large circles represent S and small circles Yb. All atoms at $y/b = 0$ or $\frac{1}{2}$ (open and filled circles). The 4 Yb^{2+} trigonal prism sites per unit cell are labelled 1, 2, 3 and 4 respectively.

in terms of ordering of the vacant trigonal prism sites. Such occupational density modulation, however, would almost certainly be accompanied by periodic structural modulation as occurs, for example, in the intermediate plagioclase feldspars (Toman and Frueh 1976).

The purpose of this paper is, firstly, to report the existence of an extinction condition left unreported in the previous electron diffraction study and, secondly, to use the extinction conditions associated with the observed incommensurate satellite reflections to provide a crystallographic description of the modulated structure.

2. Electron diffraction data

The earlier electron diffraction study identified four distinct sets of satellite reflections (Otero-Diaz and Hyde 1983), which were labelled e_1, f_1, e_2 and f_2 in analogy with the analysis of diffraction patterns from the plagioclase feldspars and a number of other such systems (see, for example, McLaren 1978). They correspond to satellite reflections of the first, second, third and fourth order respectively. The primary modulation wavevector (when folded into the first Brillouin zone (BZ) of the average structure) was given by $\boldsymbol{q}_{e1} = (1/2 - 1/\Delta)\boldsymbol{b}^*$, where Δ was composition dependent but with an average value of ~ 8. The f_1, e_2 and f_2 satellites correspond to second, third and fourth higher order satellite reflections respectively (see figure 2).

In superspace formalism, a four integer (h, k, l, m) $(\equiv h\boldsymbol{a}^* + k\boldsymbol{b}^* + l\boldsymbol{c}^* + m\boldsymbol{q}_{e1})$ schema is used to index satellite reflections. Using this schema, and for the choice of $\boldsymbol{q}_{e1}$ given above, the [001] zone axis extinction rule is given by

$$F(h, k, 0, m) = 0 \qquad \text{unless } h + m = 2n. \tag{1}$$

Notice that this extinction condition does not change if $\boldsymbol{q}_{e1}$ is replaced by $\pm\boldsymbol{q}_{e1} + n\boldsymbol{b}^*$ (n is an integer).

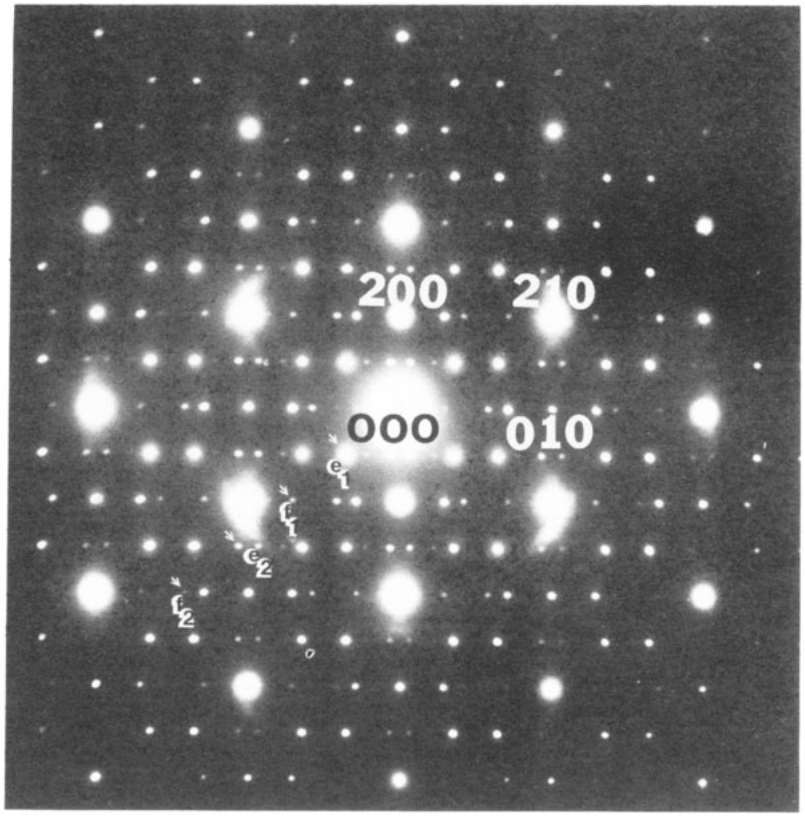

Figure 2. [001] zone axis electron diffraction pattern of the Yb_3S_4 subcell. The e_1, f_1, e_2 and f_2 satellites are marked.

To determine under which irreducible representation (of the little co-group of the modulation wave-vector) the various modulations transform (or equivalently to determine the superspace group), it is necessary, however, to have not only the [001] zone axis electron diffraction pattern but also [100] zone axis patterns. Figure 3 shows such a [100] zone axis convergent beam electron diffraction pattern (CBP) and a corresponding selected beam electron diffraction pattern (SADP). The e_1 and f_1 satellites of figure 2 are marked. The third and fourth order harmonics (e_2 and f_2 satellites) are barely visible at this zone axis.

The extinction condition in superspace formalism, for the choice of $\boldsymbol{q}_{c1}$ given above, is

$$F(0, k, l, m) = 0 \qquad \text{unless } k + l = 2n. \tag{2}$$

Notice, however, that this extinction becomes

$$F(0, k, l, m) = 0 \qquad \text{unless } k + l + m = 2n \tag{3}$$

if $\boldsymbol{q}_{e1}$ is replaced by $\boldsymbol{b}^* - \boldsymbol{q}_{e1}$ i.e. the extinction condition is dependent upon the choice of primary modulation wave-vector.

It should be pointed out that the effect of zero-order Laue zone multiple scattering by matrix reflections at both the [100] and [001] zone axis is simply to re-distribute

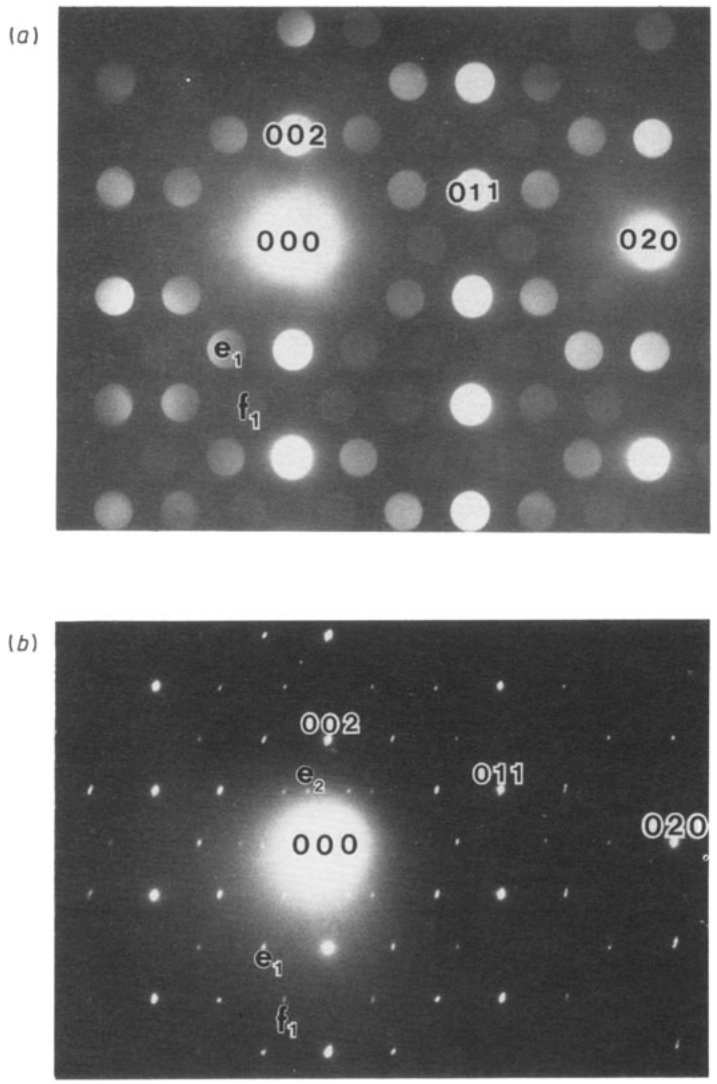

Figure 3. (*a*) A [100] zone axis convergent beam electron diffraction pattern and (*b*) its corresponding selected area diffraction pattern. The e_1 and f_1 satellites are marked.

intensity among the kinematically allowed satellite reflections but not to destroy the observed extinction conditions. In turn, this is because the P*nma* space group symmetry of the average structure does not allow zero-order Laue zone matrix reflections linking allowed and forbidden satellite reflections at either zone axis. It might be thought that the observation of second, third and fourth higher order diffraction harmonics implies that the modulation is rather non-sinusoidal in character. This, however, is not necessarily the case. For electron diffraction, the problem of disentangling the contributions to the intensity observed at higher order (f_1, e_2, f_2) satellite positions from genuine modulations (with wave-vectors $\boldsymbol{q}_{f1}$, $\boldsymbol{q}_{e2}$, and $\boldsymbol{q}_{f2}$ respectively) as opposed to contributions resulting from either multiple scattering or higher order structure factor effects is a

rather complicated problem (Bird and Withers 1986), and hence such speculations must await the results of a full x-ray structural determination. Nevertheless, it remains true to say that the mode amplitude associated with any genuine higher order modulation must transform under appropriate symmetry operations in such a way that the observed extinction conditions are obeyed.

3. Interpretation of electron diffraction data

3.1. Super-space group approach

From figures 2 and 3, it is a straightforward deduction that the (3 + 1) dimensional Bravais class is $P^{Pmmm}_{1\,\bar{1}\,1}$ (No 9). There are only two possible super-space groups with this Bravais class listed in the tables of de Wolff *et al* (1981). These are $P^{Pnma}_{1\,\bar{1}\,1}$ (62B.9.1) and $P^{Pnma}_{1\,\bar{1}\,s}$ (62B.9.2). Note that the modulation axis for orthorhombic groups is always taken to be along $\boldsymbol{c}^*$ in the super-space group tables of de Wolff *et al* (1981). The Bravais class and the two possible super-space groups are thus listed as $P^{Pmmm}_{1\,1\,\bar{1}}$, $P^{Pbnm}_{1\,1\,\bar{1}}$ and $P^{Pbnm}_{s\,1\,\bar{1}}$ respectively therein.

According to table 1 of de Wolff *et al* (1981), there are no general satellite extinction conditions resulting from the Bravais class. The only special extinction conditions given for the two possible super-space groups can be obtained from table 3 of de Wolff *et al* provided allowance is made for the different space group setting. These are:

$$F(h, k, 0, m) = 0 \qquad \text{unless } h = 2n \text{ for } P^{Pnma}_{1\,\bar{1}\,1}$$

$$F(h, k, 0, m) = 0 \qquad \text{unless } h + m = 2n \text{ for } P^{Pnma}_{1\,\bar{1}\,s}$$

respectively. It is thus apparent from figure 2 that only the second super-space group is consistent with this observed extinction rule. The superspace group symmetry element responsible for this observed extinction condition is $\{\sigma_z|\frac{1}{2}(\boldsymbol{a} + \boldsymbol{c}), \tau = \frac{1}{2}\}$ in the notation of Perez-Mato *et al* (1986, 1987).

The second extinction condition observed at the [100] zone axis (see (2)) does not, however, appear in the tables of de Wolff *et al* (1981). The reason it does not appear in the table of extinction conditions is because the extinction condition depends upon the choice of primary modulation wave-vector (see (2) and (3)). Using equation (5.9) of de Wolff *et al* (1981), it can be shown that the extinction condition given in (2) implies a superspace group symmetry operation of $\{\sigma_x|\frac{1}{2}(\boldsymbol{a} + \boldsymbol{b} + \boldsymbol{c}), \tau = 0 - \boldsymbol{q}_{e1} \cdot \frac{1}{2}\boldsymbol{b}\}$ whereas that of (3) implies the operation $\{\sigma_x|\frac{1}{2}(\boldsymbol{a} + \boldsymbol{b} + \boldsymbol{c}), \tau = \frac{1}{2} - \boldsymbol{q}_{e1} \cdot \frac{1}{2}\boldsymbol{b}\}$. The appropriate superspace group is thus $P^{Pnma}_{1\,\bar{1}\,s}$ for $\boldsymbol{q}_{e1} = (1/2 - 1/\Delta)\,\boldsymbol{b}^*$ or, equivalently, $P^{Pnma}_{s\,\bar{1}\,s}$ for $\boldsymbol{q}_{e1}$ chosen to be $(1/2 + 1/\Delta)\boldsymbol{b}^*$. This confusion would not exist if the primary modulation wave-vector were constrained to lie in the first BZ. There would then be no ambiguity about the choice of superspace group. In addition, there would be no ambiguity about extinction conditions and hence the table of extinction conditions given in de Wolff *et al* (1981) could contain both observed extinction conditions.

The complete, incommensurately-modulated structure of non-stoichiometric $\sim Yb_3S_4$ is thus described crystallographically by the superspace group $P^{Pnma}_{1\,\bar{1}\,s}$, with a primary modulation wave-vector of $\boldsymbol{q}_{e1} = (1/2 - 1/\Delta)\boldsymbol{b}^*$ ($\Delta \simeq 8$ and is dependent on stoichiometry). Some superspace group symmetry elements which leave $\boldsymbol{q}_{e1}$ invariant are $\{E|\boldsymbol{0}, \tau = 0\}$, $\{\sigma_z|\frac{1}{2}(\boldsymbol{a} + \boldsymbol{c}), \tau = \frac{1}{2}\}$, $\{\sigma_x|\frac{1}{2}(\boldsymbol{a} + \boldsymbol{b} + \boldsymbol{c}), \tau = 0 - \boldsymbol{q}_{e1} \cdot \frac{1}{2}\boldsymbol{b}\}$ and $\{C_{2y}|\frac{1}{2}\boldsymbol{b}, \tau = 0 - \boldsymbol{q}_{e1} \cdot \frac{1}{2}\boldsymbol{b}\}$. Thus, for example, the compositional modulation functions (describing Yb vacancy ordering) in those trigonal prism strings linked by the space

group symmetry operation $\{\sigma_z(\frac{1}{2}(\boldsymbol{a}+\boldsymbol{c})\}$ of the average structure, i.e. strings 1 and 3 and strings 2 and 4 respectively in figure 1, are exactly one half a modulation function repeat distance out of phase.

3.2. Modulated structure approach

Just as it is possible to derive general extinction conditions for ordinary three-dimensional space groups from a knowledge of the symmetry elements present, so it is also possible to derive general extinction conditions for incommensurate satellite reflections from a knowledge of the transformation properties of the modulations associated with each independent modulation wave-vector (Perez-Mato *et al* 1986, Withers *et al* 1987).

In general, the displacive component of the deviation from average symmetry due to the variation modulations (e_1, f_1, ...) can be written as

$$\boldsymbol{U}_{l\kappa}(\boldsymbol{r}_l) = \mathrm{Re}\, Q_{e1}\boldsymbol{e}_\kappa(\boldsymbol{q}_{e1})\exp(2\pi\, i\boldsymbol{q}_{e1}\cdot\boldsymbol{r}_l) + \mathrm{Re}\, Q_{f1}\boldsymbol{e}_\kappa(\boldsymbol{q}_{f1})\exp(2\pi\, i\boldsymbol{q}_{f1}\cdot\boldsymbol{r}_l) + \ldots. \tag{4}$$

where $\boldsymbol{q}_{f1} = 2\boldsymbol{q}_{e1}, \ldots$, $l\kappa$ refers to the κth atom in the lth unit cell, $\boldsymbol{e}_\kappa(\boldsymbol{q})$ is a displacement eigenvector and Q_q an associated complex amplitude. The compositional component of the deviation from average symmetry can be written as

$$\delta f_{l\kappa}(\boldsymbol{r}_l) = \bar{f}_\kappa[\mathrm{Re}\, P_{e1}A_\kappa(\boldsymbol{q}_{e1})\exp(2\pi\, i\boldsymbol{q}_{e1}\cdot\boldsymbol{r}_l) + \mathrm{Re}\, P_{f1}A_\kappa(\boldsymbol{q}_{f1})\exp(2\pi\, i\boldsymbol{q}_{f1}\cdot\boldsymbol{r}_l) + \ldots] \tag{5}$$

where $\delta f_{l\kappa}(\boldsymbol{r}_l)$ represents a periodic deviation from its average value, $\bar{f}_\kappa$, of the atomic scattering factor of the κth atom site in the lth unit cell, $A_\kappa(\boldsymbol{q})$, is a compositional eigenvector and P_q its associated complex amplitude. The displacement eigenvectors $\boldsymbol{e}_\kappa(\boldsymbol{q})$ have x, y and z complex components for each of the $\kappa = 1 \rightarrow N$ atoms per unit cell, while the compositional eigenvectors, in general, are represented by $\kappa = 1 \rightarrow N$ complex numbers, one for each atom in the parent unit cell.

4. Symmetry restrictions on the modulation functions

The symmetry-constrained general form of these compositional and displacive modulation functions (equations (4) and (5)) can then be obtained via application of the observed super-space group symmetry operations. In the interests of brevity (and also because it seems clear that the primary ordering mechanism is compositional in origin) only the compositional component will be derived. In general, a compositional eigenvector, $A^j(\boldsymbol{q})$, associated with the modulation wave-vector $\boldsymbol{q}$ and irreducible representation j consists of 28 complex numbers, one for each of the $\kappa = 1$–28 independent atoms per average parent unit cell. The x-ray structural refinement of Chevalier *et al* (1967), however, makes it clear that any compositional modulation in $Yb_{3-\delta}S_4$ can only be associated with the four trigonal prism cation sites (labelled 1 to 4 in figure 1) per average parent unit cell. Thus $A^j(\boldsymbol{q})$ can be written

$$A^j(\boldsymbol{q}) = (A^j_1(\boldsymbol{q}), A^j_2(\boldsymbol{q}), A^j_3(\boldsymbol{q}), A^j_4(\boldsymbol{q})).$$

The relationships between these four complex eigenvector components for each modulation harmonic can then be deduced from the observed superspace group. Thus, for

example, the superspace group symmetry operation $\{\sigma_x|\frac{1}{2}(\boldsymbol{a}+\boldsymbol{b}+\boldsymbol{c})+m\boldsymbol{a}+p\boldsymbol{c}, \tau = 0 - \boldsymbol{q}_{e1}\cdot\frac{1}{2}\boldsymbol{b}\}$ implies that

$$A_1(\boldsymbol{q}_{e1}) = A_4(\boldsymbol{q}_{e1})\,e^{-i\boldsymbol{q}_{e1}\cdot\boldsymbol{b}/2}$$
$$A_1(\boldsymbol{q}_{f1}) = A_4(\boldsymbol{q}_{f1})\,e^{-i2\boldsymbol{q}_{e1}\cdot\boldsymbol{b}/2}$$
$$A_1(\boldsymbol{q}_{e2}) = A_4(\boldsymbol{q}_{e2})\,e^{-i3\boldsymbol{q}_{e1}\cdot\boldsymbol{b}/2}$$
$$A_1(\boldsymbol{q}_{f2}) = A_4(\boldsymbol{q}_{f2})\,e^{-i4\boldsymbol{q}_{e1}\cdot\boldsymbol{b}/2}$$

The final form of this compositional deviation from average symmetry is thus given by:

$$\begin{aligned}\delta f_{1/\kappa=1,3}(\boldsymbol{r}_l) &= \pm\bar{f}_\kappa A_1\cos[2\pi\boldsymbol{q}_{e1}\cdot(\boldsymbol{r}_l - \tfrac{1}{4}\boldsymbol{b}) + 90° + \theta_1]\\ \delta f_{1/\kappa=2,4}(\boldsymbol{r}_l) &= \mp\bar{f}_\kappa A_1\cos[2\pi\boldsymbol{q}_{e1}\cdot(\boldsymbol{r}_l + \tfrac{1}{4}\boldsymbol{b}) + 90° + \theta_1]\end{aligned} \tag{6}$$

for the primary modulation (wave-vector $\boldsymbol{q}_{e1} = (\frac{1}{2} - 1/\Delta)\boldsymbol{b}^*$) (Here $\kappa = 1$ corresponds to the + sign, $\kappa = 3$ to the − sign etc.)

$$\begin{aligned}\delta f_{l,\kappa=1,3}(\boldsymbol{r}_l) &= -\bar{f}_\kappa A_2\cos[2\pi\boldsymbol{q}_{f1}\cdot(\boldsymbol{r}_l - \tfrac{1}{4}\boldsymbol{b}) + \theta_2]\\ \delta f_{l,\kappa=2,4}(\boldsymbol{r}_l) &= -\bar{f}_\kappa A_2\cos[2\pi\boldsymbol{q}_{f1}\cdot(\boldsymbol{r}_l + \tfrac{1}{4}\boldsymbol{b}) + \theta_2]\end{aligned} \tag{7}$$

for any secondary modulation (wave-vector $\boldsymbol{q}_{f1} = 2\boldsymbol{q}_{e1}$)

$$\begin{aligned}\delta f_{l,\kappa=1,3}(\boldsymbol{r}_l) &= \pm\bar{f}_\kappa A_3\cos[2\pi\boldsymbol{q}_{e2}\cdot(\boldsymbol{r}_l - \tfrac{1}{4}\boldsymbol{b}) + \theta_3 + 90°]\\ \delta f_{l,\kappa=2,4}(\boldsymbol{r}_l) &= \mp\bar{f}_\kappa A_3\cos[2\pi\boldsymbol{q}_{e2}\cdot(\boldsymbol{r}_l + \tfrac{1}{4}\boldsymbol{b}) + \theta_3 + 90°]\end{aligned} \tag{8}$$

for any third-order modulation (wave-vector $\boldsymbol{q}_{e2} = 3\boldsymbol{q}_{e1}$), etc.

The task of a full x-ray structure determination is to evaluate the (real) amplitudes and phases of these various harmonics as well as their displacive counterparts.

5. Discussion

In thinking about the modulated $Yb_{3-\delta}S_4$ structure, it is important to recognise that the compositional and displacement eigenvectors associated with each modulation wave-vector (as well, quite probably, as the valence of the Yb atoms in the trigonal prism sites) represent statistically averaged behaviour over all the (formally) equivalent sites in the plane perpendicular to the modulation wave-vector. Thus a vacancy in a particular trigonal prism site, for example, does not imply a vacancy at all those formally equivalent sites separated by lattice vectors of the basic structures in the $\boldsymbol{a}$–$\boldsymbol{c}$ plane. What the eigenvectors represent is the statistically averaged behaviour over such $\boldsymbol{a}$–$\boldsymbol{c}$ planes.

It should be noted that the phase shifts between the modulations localised on the various trigonal prism strings correspond to shifts of an anharmonic wave-form through a certain proportion of the wave-form wavelength (see, for example, de Wolff 1984). Thus the π-phase shift between the modulation components localised near strings 1 and 3, for example, refers to a half wavelength shift of the (anharmonic) wave-form in going from string 1 to string 3. It does not imply, for example, a matched expansion/contraction of the YbS_6 trigonal prisms at positions 1 and 3. Such detail would require knowledge of the full anharmonic wave-form, as represented by (6) and (8) (and their displacive counterparts) as given in the previous section, i.e. it would require a full x-ray structure determination.

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