MOCK, S., SCHRÖDER, A., SERENI, J., SIECK, M. & LÖHNEYSEN, H. V. (1993). In preparation.

NELSON, J. B. & RILEY, D. P. (1945). Proc. Phys. Soc. 57, 160–177.

ONUKI, Y., SHIBUTANI, K., HIRAI, T., KOMATSUBARA, T., SUMIYAMA, A., ODA, Y., NAGANO, H., SATO, H. & YONEMITSU, K. (1985). J. Phys. Soc. Jpn, 54, 2804–2807.

ONUKI, Y., SHIBUTANI, K., YAMAZAKI, T., KOMATSUBARA, T., MAEZAWA, K. & WAKABAYASHI, S. (1987). J. Magn. Magn. Mater. 63/64, 306–308.

ROSSAT-MIGNOD, J., REGNAULT, L. P., JACOUD, J. L., VETTIER, C., LEJAY, P., FLOUQUET, J., WALKER, E., JACCARD, D. & AMATO, A. (1988). J. Magn. Magn. Mater. 76/77, 376–384.

SCHLAGER, H. G., SCHRÖDER, A., WELSCH, M. & LÖHNEYSEN, H. V. (1993). J. Low Temp. Phys. 90, 181–204

SCHRÖDER, A., SCHLAGER, H. G. & LÖHNEYSEN, H. V. (1992). J. Magn. Magn. Mater. 108, 47–48.

SHELDRICK, G. M. (1976). SHELX76 Program for Crystal Structure Determination. Univ. of Cambridge, England.

TRAPPMANN, T. (1991). Diploma thesis, Univ. of Karlsruhe, Germany.

VILLARS, P., MATTHIS, K. & HULLIGER, F. (1989). The Structure of Binary Compounds, edited by F. R. DE BOER & D. G. PETTIFOR, pp. 1–103. Amsterdam: North-Holland.

VRTIS, M. L., JORGENSEN, J. D. & HINKS, D. G. (1986). Physica B, 136, 489–492.

A Composite Modulated Structure Approach to the Lanthanide Oxide Fluoride, Uranium Nitride Fluoride and Zirconium Nitride Fluoride Solid-Solution Fields

BY R. L. WITHERS, S. SCHMID AND J. G. THOMPSON

Research School of Chemistry, Australian National University, Canberra, ACT 0200, Australia

Abstract

It is shown that the only generally applicable crystallographic approach to the anion excess, fluorite-related solid-solution fields reported in the zirconium nitride fluoride, uranium nitride fluoride and lanthanide oxide fluoride systems is a composite modulated structure approach. A TEM and powder XRD study has been made of the ZrN_xF_{4-3x} (0.906 $< x <$ 0.936) system. The appropriate superspace-group symmetries characterizing the Q and H substructures (and indeed the entire composite modulated structure) are shown to be $P:Abmm:1s\bar{1}$ ($a_Q \approx 5.2$, $b_Q \approx 5.4$, $c_Q \approx 5.4$ Å, $\mathbf{q}_Q = -\mathbf{c}_Q{}^* + [\mathbf{c}_H{}^* - \mathbf{c}_Q{}^*]$) if the description used is based upon the Q sub-structure and $B:Pmcm:s1\bar{1}$ $\{a_H = a_Q \approx 5.2$, $b_H = \frac{1}{2}b_Q \approx 2.7$, $c_H = (p/q)c_Q$ ($p < q$) $\approx 0.845 c_Q \approx 4.56$ Å, $\mathbf{q}_H = \frac{1}{2}\mathbf{b}_H{}^* + [\mathbf{c}_H{}^* - \mathbf{c}_Q{}^*]\}$ if the description used is based upon the H sub-structure. The relationships between the reciprocal lattices of the component sub-structures are given by $\mathbf{a}_H{}^* = \mathbf{a}_Q{}^*$, $\mathbf{b}_H{}^* = 2\mathbf{b}_Q{}^*$ and $\mathbf{c}_H{}^* \approx 1.183 \mathbf{c}_Q{}^*$. Fourier decomposition of the previously reported conventional superstructure refinement of one member of this solid-solution field, $Zr_{108}N_{98}F_{138}$, has provided both underlying parent sub-structures as well as an approximation to the atomic modulation functions (AMF's) describing the mutual influence of the two parent sub-structures upon each other. In addition, such a Fourier decomposition has given an indication of the sorts of problems that will inevitably be encountered in accurately determining the appropriate AMF's when

a conventional superstructure refinement of such composite modulated structures is attempted.

1. Introduction

At an anion to cation ratio around 2.10–2.20 (*i.e.* $\sim MX_{2.10}$ to $MX_{2.20}$) an anion excess, fluorite-related solid-solution field, within which each and every composition has its own unique (but closely related) structure, has been reported in the zirconium nitride fluoride, uranium nitride fluoride and (a range of) lanthanide oxide fluoride systems (Abaouz, 1988; Mann & Bevan, 1972; Jung & Juza, 1973). Based upon several reported structure refinements (Bevan & Mann, 1975; Bevan, Mohyla, Hoskins & Steen, 1990; Jung & Juza, 1973) within the above solid-solution fields, Makovicky & Hyde (1981, 1992) and Hyde & Andersson (1989) described such systems as vernier or misfit-layer structures in which pseudo-tetragonal unit layers of edge-connected $\{X\}M_4$ tetrahedra (consisting of a 4^4 net of anions sandwiched between similar, but lower density, nets of cations *i.e.* a {100} layer of fluorite type) alternate with pseudo-hexagonal 3^6 nets of anions (see Fig. 1). The most extensively studied of such solid-solution fields is the YO_xF_{3-2x} (0.78 $< x <$ 0.87) system. Phase-analysis studies of this system by Mann & Bevan (1972) showed that each and every composition within the stoichiometric range $YX_{2.12}$ to $YX_{2.22}$ ($X = O$, F) had its own unique structure *i.e.* no diphasic regions could be detected within

this composition range. The work of Jung & Juza (1973) suggests that the same is true for the ZrN_xF_{4-3x} (0.906 < x < 0.936) system. It is therefore clear that a generally applicable crystallographic description of such systems should be based upon a composite modulated structure approach (Janner & Janssen, 1980; Withers, Thompson & Hyde, 1991;

(a)

(b)

Fig. 1. (a) The *Abmm*, $a_Q = 5.186$, $b_Q = 5.368$, $c_Q = 5.374$ Å, parent Q sub-structure obtained from the Jung & Juza (1973) structure refinement of $Zr_{108}N_{98}F_{138}$. The two Zr and two anion sites per primitive parent unit cell are labelled $M1$, $M2$ and $A1$, $A2$ (site symmetries $2mm$, $2mm$, 222 and 222) with fractional co-ordinates given by -0.191, $\frac{1}{4}$, $\frac{1}{4}$; 0.191, $\frac{3}{4}$, $\frac{1}{4}$ and 0, 0, 0; 0, $\frac{1}{2}$, 0, respectively. (b) The *Pmcm* (but very nearly *Ammm*), $a_H = a_Q = 5.186$, $b_H = \frac{1}{2}b_Q = 2.684$, $c_H = \frac{27}{32}c_Q = 4.534$ Å, parent H sub-structure obtained from the Jung & Juza (1973) structure refinement of $Zr_{108}N_{98}F_{138}$. The two anions per unit cell are labelled $A1$ and $A2$ (site symmetries $m2m$ and $m2m$) with fractional coordinates given by $\frac{1}{2}$, $-\frac{1}{4} + 0.00069$, 0 and $\frac{1}{2}$, $\frac{1}{4}$ -0.00069, $\frac{1}{2}$, respectively. Note that *Ammm* space-group symmetry for the parent H sub-structure would result if the very small shifts corresponding to the arrows in (b) and of magnitude $0.00069b_H$ according to Jung & Juza (1973) were put to zero.

van Smaalen, 1989, 1991*a,b*, 1992) rather than upon conventional crystallographic structure refinement at those special compositions for which a superstructure approximation can, apparently validly, be made (Bevan, Mohyla, Hoskins & Steen, 1990; Thompson, Withers, Sellar, Barlow & Hyde, 1990).

Composite modulated structures consist of two (or more) in general mutually incommensurable parent sub-structures, each of which is characterized by its own three-dimensional space group. In this case, the two parent sub-structures consist of a three-dimensional pseudo-tetragonal (Q) parent sub-structure (based upon the above pseudo-tetragonal unit layers of edge-connected $\{X\}M_4$ tetrahedra) and a three-dimensional pseudo-hexagonal (H) parent sub-structure (based upon the above pseudo-hexagonal 3^6 nets of anions). The mutual influence of these two parent sub-structures upon each other leads to incommensurate modulation of the ideal fractional coordinates of both (Withers, Thompson & Hyde, 1991; van Smaalen, 1992). Complete structural characterization of such systems requires refinement of both parent sub-structures as well as of the atomic modulation functions (AMF's; Pérez-Mato, Madariaga, Zúñiga & Garcia Arribas, 1987) describing the mutual influence of the two parent sub-structures upon each other.

The purpose of this paper is twofold: firstly, to determine the appropriate superspace-group symmetry for such systems from the results of a TEM study of the ZrN_xF_{4-3x} (0.906 < x < 0.936) system [the YO_xF_{3-2x} (0.78 < x < 0.87) system is not particularly stable to electron-beam irradiation] and, secondly, to provide approximations to the structural parameters allowed by this symmetry (and required for the characterization of such composite modulated structures) via Fourier decomposition of the previously reported crystal structure refinement of $Zr_{108}N_{98}F_{138}$ (Jung & Juza, 1973).

2. Experimental

2.1. Synthetic

Synthesis of ZrN_xF_{4-3x} specimens for TEM investigation was carried out following the route given by Jung & Juza (1973).

2.2. Electron diffraction

Fig. 2 shows typical (a) $[100]_Q$, (c) $[010]_Q$ and (d) $[001]_Q$ micro-diffraction patterns of specimens from within the ZrN_xF_{4-3x} (0.906 < x < 0.936) solid-solution field. The parent Q and H sub-structure reflections are indexed. Fig. 2(b) shows a $[100]_Q$ selected-area electron diffraction pattern (SADP) corresponding to Fig. 2(a). A four-integer schema based upon the Q sub-structure is used for indexing.
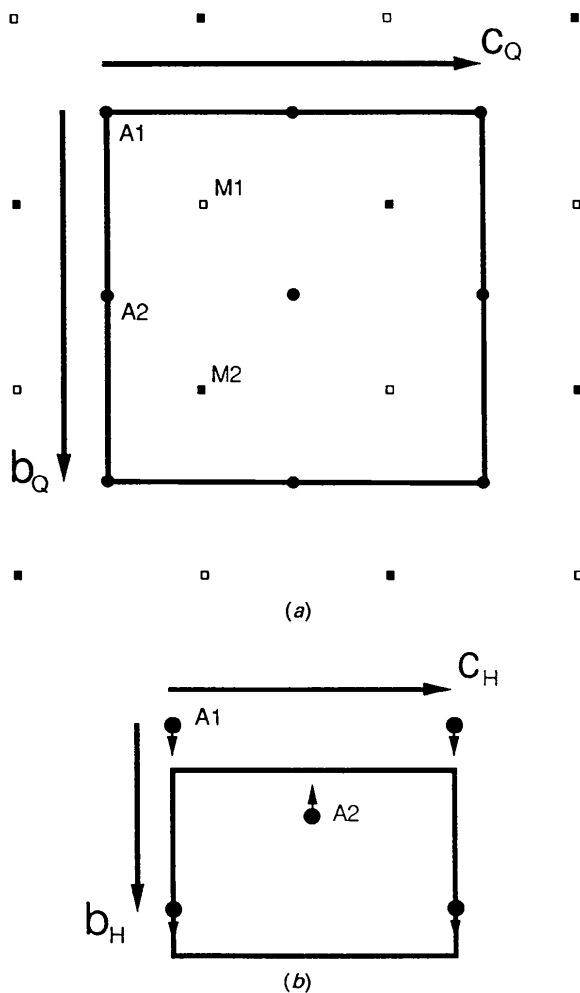
Reciprocal space tends to be dominated by a conspicuous set of strong matrix reflections, $G_Q = (h,k,l)_Q^*$, corresponding to the metrically orthorhombic pseudo-tetragonal Q parent sub-structure ($a_Q \simeq 5.2$, $b_Q \simeq 5.4$, $c_Q \simeq 5.4$ Å). The extinction conditions characteristic of this pseudo-tetragonal, Q, parent sub-structure require an average structure space-group symmetry of at least $Ab - -$. There also exists a somewhat weaker set of matrix reflections corresponding to the (also metrically orthorhombic) pseudo-hexagonal, H, parent sub-structure. The extinction conditions characteristic of this pseudo-hexagonal, H, parent sub-structure require an average structure space-group symmetry of at least $P-c-$ with $\mathbf{a}_H = \mathbf{a}_Q$, $\mathbf{b}_H = \frac{1}{2}\mathbf{b}_Q$ and $\mathbf{C}_H = (p/q)\mathbf{c}_Q$ [with p/q continuously variable although always with $q > p$]. In the case of $Zr_{108}N_{98}F_{138}$ (Jung & Juza, 1973), $p = 27$ and $q = 32$, in the case of $Y_7O_6F_9$ (Bevan & Mann, 1975), $p = 7$ and $q = 8$ while, in the case of $Y_6O_5F_8$ (Bevan, Mohyla, Hoskins & Steen, 1990), $p = 6$ and $q = 7$. In general, however, p/q is not rational. Given the misfit-layer description of Makovicky & Hyde (1992) in terms of 4^4 and 3^6 anion nets, one might have expected the parent Q and H sub-structures to have $Abmm$ and $Ammm$

space-group symmetries [with $a_H = a_Q$, $b_H = \frac{1}{2}b_Q$, $c_H = (p/q)c_Q$ ($p < q$); see Fig. 1] respectively.

The interaction of these two mutually incommensurable parent sub-structures leads to modulation of the fractional coordinates of both (de Wolff, 1988). The primary modulation wavevector, $\mathbf{q}_Q$, characteristic of the modulation of the parent Q sub-structure is given by $\mathbf{Q}_Q = (011)_H^* - (011)_Q^* = \mathbf{b}_Q^* + (\mathbf{c}_H^* - \mathbf{c}_Q^*)$ which is equivalent to $-\mathbf{c}_Q^* + (\mathbf{c}_H^* - \mathbf{c}_Q^*)$ when folded back within the first Brillouin zone (see Fig. 3a; de Wolff, 1974). This folding back of the primary modulation wavevector $\mathbf{q}_Q$ is done so as to be compatible with the superspace-group symmetry conventions of de Wolff, Janssen & Janner (1981). Similarly, the primary-modulation wavevector, $\mathbf{q}_H$, characteristic of the modulation of the parent H sub-structure, is given by $\mathbf{q}_H = (011)_H^* - (011)_Q^* = \frac{1}{2}\mathbf{b}_H^* + (\mathbf{c}_H^* - \mathbf{c}_Q^*)$. Such a primary-modulation wavevector falls on the first Brillouin zone boundary of the parent H sub-structure (see Fig. 3b) and hence, unlike for the Q sub-structure, does not need folding back. Both Q and H parent sub-structures become incommensurately modulated and each sub-structure makes a contribution to the intensity of any particular Bragg reflection.
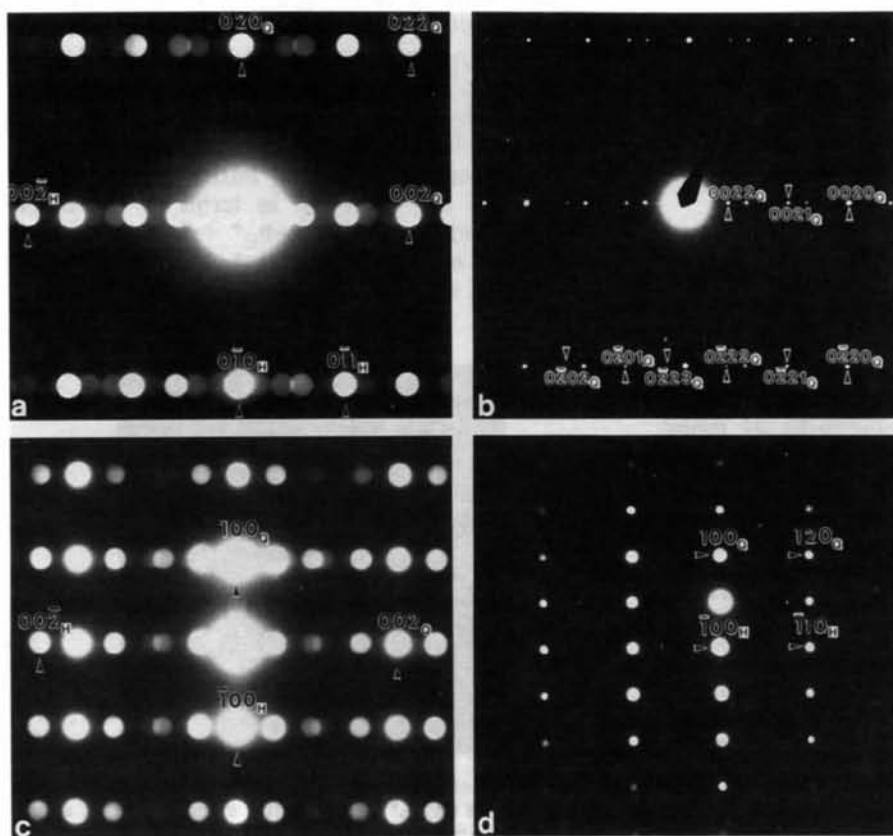

Fig. 2. Typical (a) $[100]_Q$, (c) $[010]_Q$ and (d) $[001]_Q$ microdiffraction patterns of specimens from within the ZrN_xF_{4-3x} ($0.906 < x < 0.936$) solid-solution field. The parent Q and H sub-structure reflections are indexed. (b) shows a $[100]_Q$ selected-area electron diffraction pattern (SADP) corresponding to (a). A four-integer schema, $(h,k,l,m)_Q^* = h\mathbf{a}_Q^* + k\mathbf{b}_Q^* + l\mathbf{c}_Q^* + m\mathbf{q}_Q^*$, based upon the Q sub-structure, is used for indexing.

The superspace-group symmetry (de Wolff, Janssen & Janner, 1981) of the Q sub-structure (and indeed of the whole composite modulated structure if the description is based upon the Q sub-structure) required by the observed extinction conditions is at least $P{:}Abm2{:}1ss$ [No. 39b.15.4 of Table 2 of de Wolff, Janssen & Janner (1981)]. The higher symmetry superspace group $P{:}Abmm{:}1s\bar{1}$ [No. 67b.15.4 of Table 2 of de Wolff, Janssen & Janner (1981)] is also compatible with the observed extinction conditions. Convergent-beam electron diffraction patterns
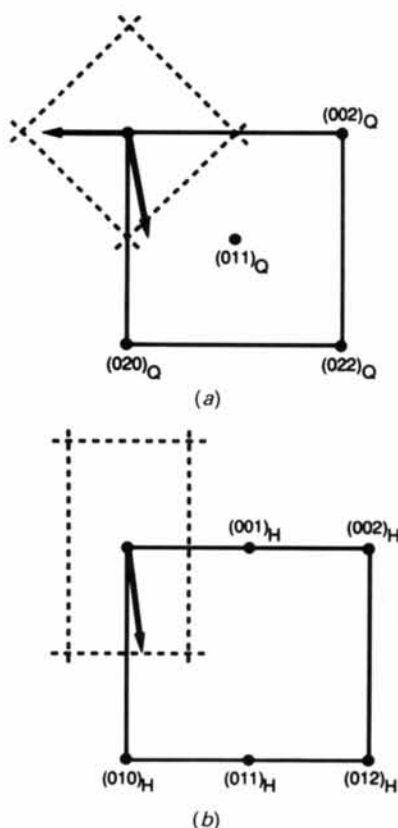

(a)

(b)

Fig. 3. (a) Two equivalent choices (arrowed) for the primary modulation wavevector, $\mathbf{q}_Q$, characteristic of the modulation of the parent Q sub-structure with respect to the reciprocal lattice of the underlying parent Q sub-structure. The first choice, given by $\mathbf{q}_Q = (011)_H{}^* - (011)_Q{}^* = \mathbf{b}_Q{}^* + (\mathbf{c}_H{}^* - \mathbf{c}_Q{}^*)$ falls outside the first Brillouin zone (dashed lines) of the reciprocal lattice of the underlying parent Q sub-structure. The second choice, and the one used in this paper, $\mathbf{q}_Q = -\mathbf{c}_Q{}^* + (\mathbf{c}_H{}^* - \mathbf{c}_Q{}^*)$, corresponds to folding $\mathbf{q}_Q$ back within the first Brillouin zone and is done so as to be compatible with the superspace-group symmetry conventions of de Wolff, Janssen & Janner (1981). (b) The corresponding primary modulation wavevector, $\mathbf{q}_H = (011)_H{}^* - (001)_Q{}^* = \frac{1}{2}\mathbf{b}_H{}^* + (\mathbf{c}_H{}^* - \mathbf{c}_Q{}^*)$, characteristic of the modulation of the parent H sub-structure with respect to the reciprocal lattice of the underlying parent H sub-structure. Note that such a primary modulation wavevector falls on the first Brillouin zone boundary (dashed lines) of the reciprocal lattice of parent H sub-structure and hence does not need folding back.

(CBP's) taken with the $(001)_Q{}^*$ systematic row excited (see, for example, Fig. 4), however, strongly suggest the presence of mirror symmetry perpendicular to the $\mathbf{c}_Q{}^*$ direction of reciprocal space and hence imply that the appropriate superspace-group symmetry is $P{:}Abmm{:}1s\bar{1}$. The corresponding characteristic extinction conditions are as follows:

$$F(h,k,l,m)_Q = 0 \quad \text{unless} \quad k+l = 2n \quad \text{(see Fig. 2)}$$

$$F(0,k,l,m)_Q = 0 \quad \text{unless} \quad k,l = 2n \quad \text{(see Fig. 2a)}$$

$$F(h,0,l,m)_Q = 0 \quad \text{unless} \quad l,m = 2n \quad \text{(see Fig. 2c)}.$$

Similarly the superspace-group symmetry of the H sub-structure (and indeed of the whole composite modulated structure if the description is based upon the H sub-structure) required by the observed extinction conditions is at least $B{:}Pmc2_1{:}s1s$ [No. 26a.10.2 of Table 2 of de Wolff, Janssen & Janner (1981)] but again most probably (see Fig. 4), $B{:}Pmcm{:}s1\bar{1}$ [No. 51c.10.2 of Table 2 of de Wolff, Janssen & Janner (1981)]. The corresponding characteristic extinction conditions are:

$$F(0,k,l,m)_H = 0 \quad \text{unless} \quad m = 2n \quad \text{(see Fig. 2a)}$$

$$F(h,0,l,0)_H = 0 \quad \text{unless} \quad l = 2n \quad \text{(see Fig. 2c)}.$$

The primary modulation wavevectors characteristic of the two sub-structures chosen above must be consistent with the Bravais classes (de Wolff, Janssen & Janner, 1981) of the other. Thus, the reflection condition characteristic of the Bravais class of the Q sub-structure, *i.e.* $F(h,k,l,m)_Q{}^* = 0$ unless $k+l = 2n$, must be equivalent to the reflection condition which is characteristic of the Bravais class of the H sub-structure when the reciprocal lattice vectors of one sub-structure are expressed in terms of the other. Thus, $(h,k,l,m)_Q{}^* = h\mathbf{a}_Q{}^* + k\mathbf{b}_Q{}^* + l\mathbf{c}_Q{}^* + m\mathbf{q}_Q{}^* = [h, \frac{1}{2}(k+l) - m, l-m, 2m-l]_H{}^*$. That $F(h,k,l,m)_Q{}^* = 0$ unless $k+l = 2n$ does not place any constraint
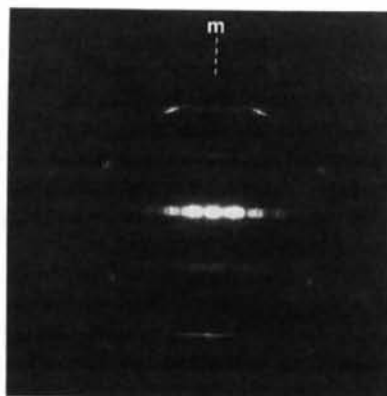

Fig. 4. A typical convergent-beam electron diffraction pattern taken with the $(001)_Q{}^*$ systematic row excited. Note the apparent mirror plane perpendicular to $(001)_Q{}^*$.

upon the H sub-structure *i.e.* it is entirely compatible with the $Pmcm$ space-group symmetry of the average H sub-structure. Note, however, that this would no longer be the case if the average H sub-structure had $Ammm$ rather than $Pmcm$ space-group symmetry. This lowering of the average structure space-group symmetry of the H sub-structure from $Ammm$ to $Pmcm$ corresponds to an induced $\mathbf{q} = \mathbf{b}^*$ displacive modulation and allows $\mathbf{b}_H$ axis motion in opposite directions of the two distinct anions per unit cell (see the arrows in Fig. 1b). The H sub-structure is thus moved at least some way from a 3^6 net back towards a 4^4 net. The extent of this motion, however, can only be determined from structure refinement.

Given the experimental observation of a continuous smooth variation of $\mathbf{q}_Q$ and $\mathbf{q}_H$ across the whole solid-solution field within the ZrN_xF_{4-3x} ($0.906 < x < 0.936$) and YO_xF_{3-2x} ($0.78 < x < 0.87$) systems (*i.e.* the lack of any evidence for q/p 'locking in' to rational fractions such as $\frac{32}{27}, \frac{7}{6}, \frac{8}{7}, \frac{5}{4}...$), it is clear that a generally applicable crystallographic description of such phases must be based upon a modulated structure, or superspace group, approach rather than upon conventional crystallographic structure refinement at rational values of q/p. In general, $\mathbf{q}_Q$ and $\mathbf{q}_H$ are incommensurable with respect to the reciprocal lattices of their corresponding sub-structures. For rational values of q/p, however, it appears that a superstructure approximation can be made and a conventional three-dimensional structure refinement attempted. Several such structure refinements have been carried out within the YO_xF_{3-2x} ($0.78 < x < 0.87$) system and one within the ZrN_xF_{4-3x} ($0.906 < x < 0.936$) system.

In the remainder of this paper the reported crystal structure refinement of $Zr_{108}N_{98}F_{138}$ (Jung & Juza, 1973) is Fourier decomposed into its two constituent modulated structures – one corresponding to the Q sub-structure and the other to the H sub-structure. Both these Q and H sub-structures possess well defined, underlying, parent structures which it is reasonable to presume should remain fairly constant across the whole of the solid-solution field. Fourier decomposition of the reported structure refinements in terms of these parent structures and their accompanying displacive modulations enables a picture to be built up of the whole of the solid-solution field provided we make the reasonable assumption that only the modulation wavevectors, and not the corresponding displacement eigenvectors, vary substantially across the solid-solution field.

3. The underlying parent sub-cells of $Zr_{108}N_{98}F_{138}$

As mentioned above, given the misfit layer description of Makovicky & Hyde (1992), one might have expected the parent Q and H sub-structures to have

$Abmm$ and $Ammm$ space-group symmetries [with $a_H = a_Q$, $b_H = \frac{1}{2}b_Q$, $c_H = (p/q)c_Q$ ($p < q$); see Fig. 1] respectively. In the case of $Zr_{108}N_{98}F_{138}$ (Jung & Juza, 1973), $p = 27$, $q = 32$ and $32c_H = 27c_Q$. Fourier decomposition and appropriate re-setting of the reported crystal structure of $Zr_{108}N_{98}F_{138}$ (Jung & Juza, 1973) in such terms gives an $Ab2m$ (but very nearly $Abmm$), $a_Q = 5.186$, $b_Q = 5.368$ and $c_Q = 5.374$ Å average Q structure and a $Pmcm$ (but very nearly $Ammm$), $a_H = a_Q = 5.186$, $b_H = \frac{1}{2}b_Q = 2.684$, $c_H = \frac{27}{32}c_Q = 4.534$ Å average H structure (with the -c- glide located at $y = -0.00303$). However, the extinction conditions characteristic of the whole solid-solution series given above require the parent structures of both the Q and H sub-structures to have at least $mm2$ point-group symmetry with respect to the same origin. This is consistent with an underlying parent Q space-group symmetry of $Abmm$ but not with $Ab2m$.

The choice of an underlying parent structure is somewhat complicated by the fact that the two sub-structures are in fact mutually commensurable – albeit at a very high order of commensurability. Thus, high-order harmonic $\mathbf{q} = 0$ displacive modulations of each of the underlying parent structures due to their interaction with the other structure and resulting in a lowered average structure space-group symmetry are technically allowed (see §2 of Pérez-Mato, Madariaga, Zúñiga & Garcia Arribas, 1987). In particular, a 27th order harmonic of $\mathbf{q}_Q (= -\frac{22}{27}\mathbf{c}_Q^*)$ allows an origin shift along the $\mathbf{b}_Q$ axis for the oxygen and metal sub-lattices of the parent Q structure which need not be equal. Fourier decomposition of the reported crystal structure gives these parameters as $0\mathbf{b}_Q$ and $0.00030\mathbf{b}_Q$, respectively. Similarly a 32nd order harmonic of $\mathbf{q}_H$ ($= \frac{1}{2}\mathbf{b}_H^* + \frac{5}{32}\mathbf{c}_H^*$) allows an origin shift along $\mathbf{b}_H$ for the oxygen sub-lattice of the parent H structure which again need not equal either of the above parameters. It is this $\mathbf{b}_H$ shift of $-0.00606\mathbf{b}_H$ which shifts the location of the -c- glide to $y = -0.00303$. As mentioned above, however, the extinction conditions characteristic of the whole solid-solution series require the parent structures of both the Q and H sub-structures to have at least $mm2$ point-group symmetry with respect to the same origin. Thus, in what follows, we have set these three parameters to zero and taken the resultant $Abmm$ (for Q) and $Pmcm$ (for H) structures (see Fig. 1) to be the underlying parent Q and H sub-structures. If the three parameters above are genuinely non-zero, they have to be understood in terms of high-order harmonic displacive modulations of the $Abmm$ and $Pmcm$ parent sub-structures. Note that the space-group symmetry of the parent Q sub-structure would be $Ammm$ *i.e.* an ideal 3^6 oxygen array if the magnitude of the shift represented by the arrows in Fig.

1(b) were zero. Fourier decomposition of the reported crystal structure gives a magnitude for this shift of only $0.00069b_H$ and hence deviation from the ideal 3^6 geometry (according to Jung & Juza, 1973) is very slight.

4. Modulation of the parent Q and H sub-structures

Having defined the parent sub-structures, it is now necessary to allow both sub-structures to respond to the presence of the other. This response, or relaxation, takes the form of compositional and displacive modulation characterized by appropriate compositional and displacement eigenvectors and by modulation wavevectors which are harmonics of the primary modulation wavevectors already defined above. Note that Jung & Juza (1973) did not distinguish between N and F in their refinement of $Zr_{108}N_{98}F_{138}$ and hence no further consideration will be given to compositional modulation in this paper.

As recently pointed out by Pérez-Mato (1991), the number of free structural parameters to be refined in a superspace-group refinement approach to a commensurately modulated superstructure is, in principle, precisely the same as the number of free structural parameters required for a conventional superstructure approach. Thus, the conventional space-group symmetry of $Cm2a$ (equivalent to $Ab2m$ in the setting we have used) reported for $Zr_{108}N_{98}F_{138}$ by Jung & Juza (1973) has exactly the same number of free structural parameters as a structure description using superspace-group symmetries of $P:Abmm:$ $1s\bar{1}$ for the Q sub-structure and $B:Pmcm:s1\bar{1}$ for the H sub-structure. The number of effective structural parameters to be refined, however, decreases when some of the higher order harmonic modulations can be neglected for whatever reason.

The experimental observation (in the case of the ZrN_xF_{4-3x} system) that the intensity of satellite reflections drops off rapidly with increasing harmonic order so that no harmonics of higher order than third can ever be detected around the parent Bragg reflections of the Q sub-structure in X-ray powder patterns implies that the degrees of freedom associated with harmonics of order greater than three can be neglected. In the specific case of $Zr_{108}N_{98}F_{138}$, inspection of the data of Jung & Juza (1973) shows that 240 parent Q sub-structure reflections, 414 first-order, 58 second-order, 252 third-order and only eight fourth-order satellite reflections were measured with no satellite reflections of higher order than fourth being observable. As the corresponding primary modulation wavevector of the Q sub-structure $= -\frac{22}{27}c_Q{}^*$, from a conventional superstructure point of view there are, in principle, 27 separate harmonics each with several associated degrees of freedom to be refined. Given that no

harmonics of higher order than fourth could ever be detected, however, it is clear that the conventional superstructure approach is vastly over parameterized.

4.1. Modulation of the parent Q sub-structure

Given an unmodulated parent Q sub-structure space-group symmetry of $Abmm$, the little co-group (see Bradley & Cracknell, 1972) of the primary modulation wavevector q_Q $(= -\frac{22}{27}c_Q{}^*$ for $Zr_{108}N_{98}F_{138}, = -\frac{5}{6}c_Q{}^*$ for $Y_6O_5F_8, = -\frac{6}{7}c_Q{}^*$ for $Y_7O_6F_9$ and $= \gamma c_Q{}^*$, γ irrational in the general case) and all its higher order harmonics mq_Q is given by $\{E, C_{2z}, \sigma_x, \sigma_y\}$. The corresponding multiplication table is given by:

	E	C_{2z}	σ_x	σ_y
R_1	1	1	1	1
R_2	1	1	$\bar{1}$	$\bar{1}$
R_3	1	$\bar{1}$	1	$\bar{1}$
R_4	1	$\bar{1}$	$\bar{1}$	1 .

The superspace-group symmetry of the Q sub-structure (and indeed of the whole composite modulated structure) implied by the reported space-group symmetry of $Zr_{108}N_{98}F_{138}$ (Jung & Juza, 1973) and required by the observed extinction conditions is $P:Abmm:1s\bar{1}$. Such a superspace-group symmetry implies that the displacive modulations associated with all odd-order harmonics transform with R_3 symmetry whereas all even-order harmonics transform with R_1 symmetry. There are two metal atoms and two anions per primitive parent unit cell – labelled M_1, M_2 and A_1, A_2, in Fig. 1(a). An R_3 irreducible representation constrains the corresponding displacive modulations to entail only b_Q shifts for the Zr ions but allows a_Q and b_Q shifts for the anions. An R_1 irreducible representation allows a_Q and c_Q shifts for the Zr ions but only allows c_Q shifts for the anions. The atomic modulation functions (AMF's; see Pérez-Mato, Madariaga, Zúñiga & Garcia Arribas, 1987) describing the most general possible structural deviation of these Zr and (N,F) ions away from their positions in the underlying parent Q sub-cell, for the observed superspace-group symmetry of $P:Abmm:1s\bar{1}$, can then be written in the form:

$$U_{M1,2}(T_Q)$$

$$= \pm \imath_Q \sum_{2m=2,4,\ldots} \varepsilon_{Mx}(2mq_Q;R_1)$$

$$\times \cos\{0° + 2m[2\pi q_Q \cdot (T_Q + \tfrac{1}{4}c_Q) + \theta(q_Q)]\}$$

$$+ b_Q \sum_{2m+1=1,3,\ldots} \varepsilon_{My}[(2m+1)q_Q;R_3]$$

$$\times \cos\{90° + (2m+1)[2\pi q_Q \cdot (T_Q + \tfrac{1}{4}c_Q) + \theta(q_Q)]\}$$

$$+ \mathbf{c}_Q \sum_{2m=2,4,...} \varepsilon_{Mz}(2m\mathbf{q}_Q;R_1)$$

$$\times \cos\{90° + 2m[2\pi\mathbf{q}_Q \cdot (\mathbf{T}_Q + \tfrac{1}{4}\mathbf{c}_Q) + \theta(\mathbf{q}_Q)]\}$$

and

$$U_{A1,2}(\mathbf{T}_Q)$$

$$= \pm \mathbf{a}_Q \sum_{2m+1=1,3,...} \varepsilon_{Ax}[(2m+1)\mathbf{q}_Q;R_3]$$

$$\times \cos\{0° + (2m+1)[2\pi\mathbf{q}_Q \cdot \mathbf{T}_Q + \theta(\mathbf{q}_Q)]\}$$

$$+ \mathbf{b}_Q \sum_{2m+1=1,3,...} \varepsilon_{Ay}[(2m+1)\mathbf{q}_Q;R_3]$$

$$\times \cos\{90° + (2m+1)[2\pi\mathbf{q}_Q \cdot \mathbf{T}_Q + \theta(\mathbf{q}_Q)]\}$$

$$+ \mathbf{c}_Q \sum_{2m=2,4,...} \varepsilon_{Az}[(2m\mathbf{q}_Q;R_1)$$

$$\times \cos\{90° + 2m[2\pi\mathbf{q}_Q \cdot \mathbf{T}_Q + \theta(\mathbf{q}_Q)]\},$$

where $\mathbf{T}_Q$ is an allowed Bravais lattice vector of the average Q sub-structure and $\mathbf{q}_Q$ is the, in general, incommensurate primary modulation wavevector of the Q sub-structure. Note that there are only three degrees of freedom associated with each harmonic and thus, given that no harmonics of higher order than fourth can ever be detected in the ZrN_xF_{4-3x} $(0.906 < x < 0.936)$ system, only 12 degrees of freedom at most should ever be required to describe the Q sub-structure.

Formally application of the superspace-group symmetry operation $\{C_{2y}|0,0\}$ [equivalent to the twofold in the conventional $Ab2m$ space group of Jung & Juza (1973)] constrains $\theta(\mathbf{q}_Q) = 90°$. In general, we write $\theta(\mathbf{q}_Q) = 90° + \theta_0$. The global phase θ_0 is, in general (i.e. for an incommensurate $\mathbf{q}_Q$), arbitrary i.e. a parent sub-structure origin shift of $\mathbf{T}_Q$ is equivalent to changing θ_0 from θ_0 to $\theta_0 - 2\pi\mathbf{q}_Q \cdot \mathbf{T}_Q$. However, when $\mathbf{q}_Q$ is such that a superstructure approximation can be made, as for $Zr_{108}N_{98}F_{138}$, its value formally becomes important in determining the appropriate space group of the resultant superstructure. Thus, in the case of $Zr_{108}N_{98}F_{138}$, $\theta_0 = -90°$ gives rise to a resultant space-group symmetry of $A2/b11$ whereas $\theta_0 = 0°$ gives rise to the resultant space-group symmetry assumed by Jung & Juza (1973) of $Ab2m$. Formally such structures are energetically and structurally distinct and the corresponding value of θ_0 a refineable parameter. For 'long-period' modulated structures such as the ninefold superstructure of thiourea, however, it has recently been shown from refinement statistics (Pérez-Mato, 1991) that this global phase is not a refineable parameter and that such structures can be treated as incommensurate from a practical point of view. Given the small number of higher order harmonics observed in the present case in conjunction

Table 1. Q sub-structure mode amplitudes obtained from a Fourier decomposition of the reported crystal structure of $Zr_{108}N_{98}F_{138}$

m	$\varepsilon_{Mx}(m\mathbf{q}_Q)$	$\varepsilon_{My}(m\mathbf{q}_Q)$	$\varepsilon_{Mz}(m\mathbf{q}_Q)$	$\varepsilon_{Ax}(m\mathbf{q}_Q)$	$\varepsilon_{Ay}(m\mathbf{q}_Q)$	$\varepsilon_{Az}(m\mathbf{q}_Q)$
1	0	-0.0296	0	0.0344	-0.0243	0
2	0.0000	0	0.0006	0	0	0.0001
3	0	-0.0080	0	-0.0053	0.0082	0
4	0.0000	0	-0.0016	0	0	0.0006
5	0	-0.0011	0	-0.0013	-0.0029	0
6	0.0000	0	-0.0014	0	0	0.0002
7	0	-0.0004	0	-0.0000	0.0029	0
8	0.0000	0	-0.0008	0	0	0.0004
9	0	0.0008	0	0.0004	-0.0023	0
10	0.0000	0	-0.0014	0	0	-0.0000
11	0	-0.0002	0	-0.0002	0.0015	0
12	0.0000	0	-0.0011	0	0	-0.0000
13	0	0.0003	0	-0.0004	-0.0020	0
14	0.0000	0	-0.0011	0	0	-0.0003
15	0	0.0004	0	-0.0000	0.0019	0
16	0.0000	0	-0.0005	0	0	-0.0004
17	0	-0.0006	0	0.0003	-0.0013	0
18	0.0000	0	0.0004	0	0	-0.0002
19	0	0.0006	0	0.0006	0.0025	0
20	0.0000	0	0.0001	0	0	-0.0003
21	0	0.0000	0	-0.0003	-0.0019	0
22	0.0000	0	0.0008	0	0	0.0002
23	0	0.0015	0	0.0000	0.0014	0
24	0.0000	0	0.0014	0	0	0.0001
25	0	0.0004	0	0.0004	-0.0015	0
26	0.0000	0	0.0014	0	0	0.0004
27	0	-0.0003	0	0	0.0018	0

with the high order of commensurability, it therefore seems highly likely that an equally good refinement could be obtained in either of the above space groups i.e. the global phase may well not be a refineable parameter for this solid-solution field.

The highest order modulation harmonic required in the above equations in order to obtain a fit to the Jung & Juza (1973) structure refinement is determined by two requirements – firstly that the corresponding modulation wavevectors should be equivalent (i.e. relatable by an allowed average Q sub-structure reflection) and secondly that the corresponding atomic displacement pattern should transform according to the same irreducible representation. Thus, for $Zr_{108}N_{98}F_{138}$, where $\mathbf{q}_Q = -\frac{22}{27}\mathbf{c}_Q^*$, the mth and the $(54 - m)$th harmonics are equivalent and hence harmonics out to 27th order must formally be taken into account. The values of the above parameters corresponding to the Jung & Juza (1973) structure refinement are given in Table 1. Values given as 0 are constrained to be zero by symmetry. All other values can, in principle, be non-zero i.e. are superspace-group allowed. The corresponding AMF's are shown plotted as a function of $\mathbf{q}_Q \cdot (\mathbf{T}_Q + \frac{1}{4}\mathbf{c}_Q)$ (modulo an integer) for the cations in Fig. 5 and $\mathbf{q}_Q \cdot \mathbf{T}_Q$ (modulo an integer) for the anions in Fig. 6.

The first point to note about Table 1 is that all the degrees of freedom associated with $\mathbf{a}_Q$ motion of the Zr atoms are zero according to Jung & Juza (1973). It would appear that this is not the result of the

refinement (in which case one might have expected small but not identically zero modulation amplitudes) but rather represents an additional constraint to the conventional space-group symmetry imposed for some unknown reason by Jung & Juza (1973). This is confirmed by the fact that a Fourier decomposition of the reported crystal structures within the YO_xF_{3-2x} $(0.78 < x < 0.87)$ system (Bevan, Mohyla, Hoskins & Steen, 1990) gives small but non-zero values to these superspace-group-allowed degrees of freedom. The second point to note is that the modulation amplitudes for all harmonics of greater order than third are rather small [i.e. less than ~0.003 (fractional coordinates) or ~0.015 Å in magnitude] as they should be, given that no harmonics of higher order than fourth can ever be detected around parent Q sub-structure reflections in the ZrN_xF_{4-3x} $(0.906 < x < 0.936)$ system.

In a comparable study of the reported crystal structure of $Nb_2Zr_6O_{17}$ [a member of the

$Nb_2Zr_{x-2}O_{2x+1}$ $(x = 7.1-10.3)$ solid-solution field (Withers, Thompson & Hyde, 1991)], it was found by Fourier decomposition that certain superspace-group-forbidden degrees of freedom were in fact allowed by the conventional space-group symmetry used. All such superspace-group-forbidden modulation amplitudes refined to small but nonetheless non-
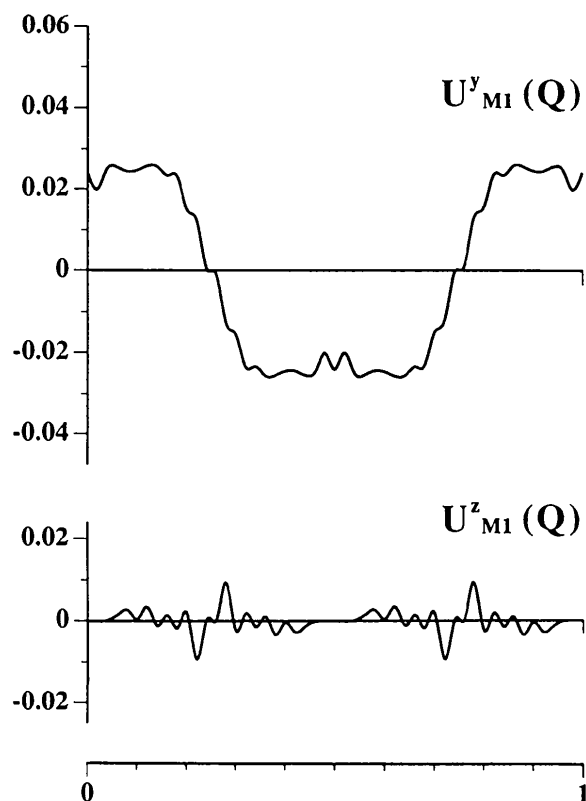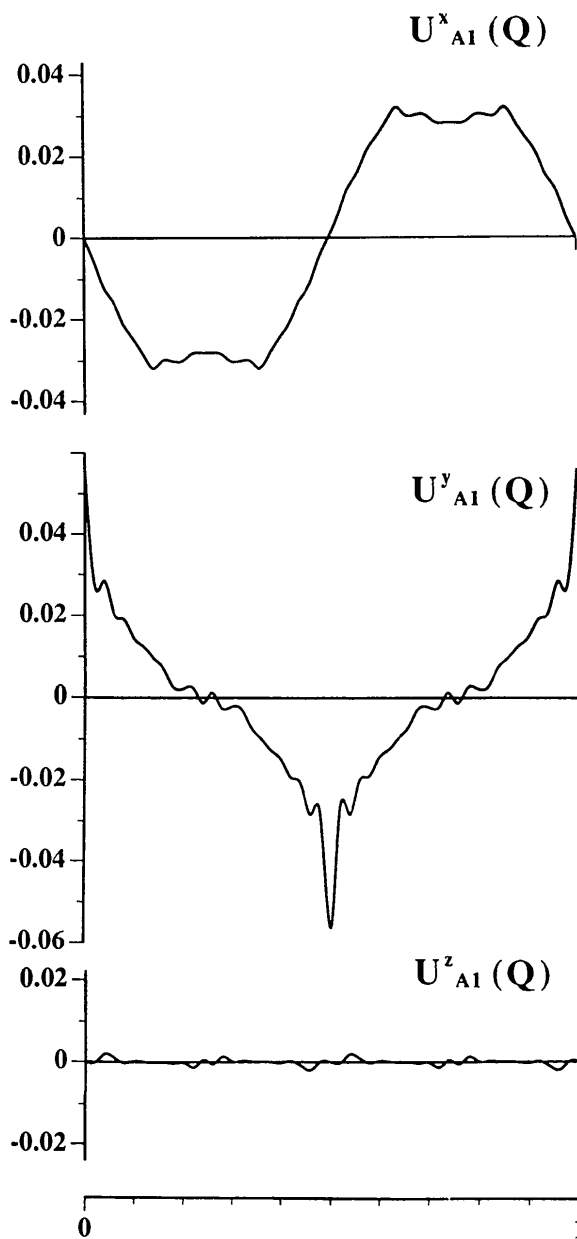

Fig. 5. A plot of the cation Q sub-structure AMF's derived from the Jung & Juza (1973) structure refinement plotted as a function of $q_Q \cdot (T_Q + \frac{1}{4}c_Q)$ (modulo an integer). The units of the ordinate axis are fractional coordinates but they have been rescaled so that the height of the appropriate AMF at any particular point is directly proportional to the corresponding shift in Å.

Fig. 6. A plot of the anion Q sub-structure AMF's derived from the Jung & Juza (1973) structure refinement plotted as a function of $q_Q \cdot T_Q$ (modulo an integer). The units of the ordinate axis are fractional coordinates but they have been rescaled so that the height of the appropriate AMF at any particular point is directly proportional to the corresponding shift in Å.

zero values. These refined superspace-group-forbidden modulation amplitudes give a measure of the uncertainty which should be ascribed to the remaining superspace-group-allowed modulation amplitudes. In that case, this measure of the uncertainty or error to be associated with the stronger scattering metal-atom modulation amplitudes corresponded to ~0.003 (fractional co-ordinates) or ~0.015 Å. Such an uncertainty or error will also apply to the modulation amplitudes for the Q sub-structure given in Table 1, *i.e.* it is highly likely that superspace-group-allowed modulation amplitudes less than ~0.003 in Table 1 might as well be put to zero and really represent 'noise' on the AMF's. In that case, only two modulation harmonics, namely the first and the third, and six associated structural parameters are required in order to define the AMF's associated with the Q sub-structure. The substantial amplitude of the third-order harmonics with respect to the first-order harmonics (see Table 1) gives the corresponding AMF's more of a 'square wave' rather than sinusoidal appearance and suggests that the structure may well be composed of domain-like regions of commensurate sub-structures separated by regions where the phase of the modulation varies rapidly. However, a much better refinement is really needed before such details can be discussed. Note that even such small-amplitude higher order harmonic modulations can sometimes give rise not just to random noise on the AMF signal but to sharp chemically implausible spikes [see the $U^y_{A1}(Q)$ AMF shown in Fig. 6]. Such spikes on the AMF's of the stronger scattering sub-structure could well be expected to cause problems in determining the AMF's associated with the weaker scattering H sub-structure. Finally note the phase relationships of the various AMF's *e.g.* the '90° out of phase' phase relationship between the $U^x_{A1}(Q)$ and $U^y_{A1}(Q)$ AMF's.

4.2. Modulation of the parent H sub-structure

Given an unmodulated parent H sub-structure space-group symmetry of $Pmcm$, the little co-group of the primary modulation wavevector $\mathbf{q}_H$ ($= \frac{1}{2}\mathbf{b}_H^* + \frac{5}{32}\mathbf{c}_H^*$ for $Zr_{108}N_{98}F_{138}$, $= \frac{1}{2}\mathbf{b}_H^* + \frac{1}{7}\mathbf{c}_H^*$ for $Y_6O_5F_8$, $= \frac{1}{2}\mathbf{b}_H^* + \frac{1}{8}\mathbf{c}_H^*$ for $Y_7O_6F_9$ and $= \frac{1}{2}\mathbf{b}_H^* + \gamma\mathbf{c}_H^*$, γ irrational in the general case) and all its higher order harmonics $m\mathbf{q}_H$ is given by $\{E, C_{2z}, \sigma_x, \sigma_y\}$. The corresponding multiplication table is given above. The superspace-group symmetry of the H sub-structure implied by the reported space-group symmetry of $Zr_{108}N_{98}F_{138}$ (Jung & Juza, 1973) and required by the electron diffraction evidence is $B:Pmcm:s1\bar{1}$. Such a superspace-group symmetry implies that the displacive modulations associated with all odd-order harmonics transform with R_4 symmetry whereas all even order harmonics trans-

form with R_1 symmetry. There are only two anions per primitive parent unit cell of the H sub-structure – labelled A_1, A_2 in Fig. 1(b). An R_4 irreducible representation constrains the corresponding displacive modulations to entail only $\mathbf{a}_H$ shifts whereas an R_1 irreducible representation allows $\mathbf{b}_H$ and $\mathbf{c}_H$ shifts. The AMF's describing the most general possible structural deviation of the (N,F) ions away from their positions in the underlying parent H sub-structure, for the observed superspace-group symmetry of $B:Pmcm:s1\bar{1}$, can then be written in the form:

$$U_{A1,2}(\mathbf{T}_H)$$

$$= \mathbf{a}_H \sum_{2m+1=1,3,\ldots} \varepsilon_{Ax}[(2m+1)\mathbf{q}_H;R_4]$$

$$\times \cos\{90° + (2m+1)[2\pi\mathbf{q}_H \cdot (\mathbf{T}_H - \pm\tfrac{1}{4}\mathbf{c}_H) + \theta(\mathbf{q}_H)]\}$$

$$\pm \mathbf{b}_H \sum_{2m=2,4,\ldots} \varepsilon_{Ay}(2m\mathbf{q}_H;R_1)$$

$$\times \cos\{0° + 2m[2\pi\mathbf{q}_H \cdot (\mathbf{T}_H - \pm\tfrac{1}{4}\mathbf{c}_H) + \theta(\mathbf{q}_H)]\}$$

$$+ \mathbf{c}_H \sum_{2m=2,4,\ldots} \varepsilon_{Az}(2m\mathbf{q}_H;R_1)$$

$$\times \cos\{90° + 2m[2\pi\mathbf{q}_H \cdot (\mathbf{T}_H - \pm\tfrac{1}{4}\mathbf{c}_H) + \theta(\mathbf{q}_H)]\}.$$

Note that there is only one degree of freedom associated with each odd-order harmonic and two degrees of freedom associated with each even-order harmonic. Application of the superspace-group symmetry operation $\{C_{2y}|0,0\}$ gives $\theta(\mathbf{q}_H) = 0° + 2\pi\mathbf{q}_H \cdot \frac{1}{4}\mathbf{c}_H$. In general we write $\theta(\mathbf{q}_H) = 0° + 2\pi\mathbf{q}_H \cdot \frac{1}{4}\mathbf{c}_H + \theta_0$, where θ_0 is the same global phase parameter defined in §4.1 above. Also as in §4.1 above, $\theta_0 = -90°$ gives rise to a resultant space-group symmetry of $A2/b11$ whereas $\theta_0 = 0°$ gives rise to the resultant space-group symmetry assumed by Jung & Juza (1973) of $Ab2m$ for $Zr_{108}N_{98}F_{138}$. Note that harmonics out to 16th order must formally be taken into account for $Zr_{108}N_{98}F_{138}$, where $\mathbf{q}_H = \frac{1}{2}\mathbf{b}_H^* + \frac{5}{32}\mathbf{c}_H^*$. The values of these parameters corresponding to the Jung & Juza (1973) refinement are given in Table 2 and the corresponding AMF's as a function of $\mathbf{q}_H \cdot \mathbf{T}_H$ (modulo an integer) in Fig. 7.

The first point to make is that the more weakly scattering H sub-structure will, of necessity, be less well determined than the more strongly scattering Q sub-structure. Therefore, a higher uncertainty needs to be ascribed to the modulation amplitudes associated with the H sub-structure. In the study of $Nb_2Zr_6O_{17}$ (Withers, Thompson & Hyde, 1991), for example, the refined superspace-group-forbidden modulation amplitudes associated with the more weakly scattering anion sub-structure corresponded to ~0.01 (fractional coordinates) or ~0.05 Å *i.e.* ~2-3 times larger than those associated with the metal-atom sub-structure. Using a similar criterion,

Table 2. *H sub-structure mode amplitudes obtained from a Fourier decomposition of the reported crystal structure of* $Zr_{108}N_{98}F_{138}$

m	$\varepsilon_{Ax}(m\mathbf{q}_H)$	$\varepsilon_{Ay}(m\mathbf{q}_H)$	$\varepsilon_{Az}(m\mathbf{q}_H)$
1	0.0617	0	0
2	0	−0.0062	−0.0196
3	0.0154	0	0
4	0	−0.0007	0.0173
5	−0.0015	0	0
6	0	−0.0061	−0.0102
7	−0.0024	0	0
8	0	−0.0018	0.0000
9	−0.0042	0	0
10	0	−0.0012	−0.0066
11	−0.0050	0	0
12	0	0.0022	−0.0153
13	−0.0027	0	0
14	0	0.0004	−0.0062
15	−0.0017	0	0
16	0.0000	0.0006	0
32	0	−0.0061	0

superspace-group-allowed modulation amplitudes less than ~0.01 in Table 2 might as well be put to zero.

There is clearly a large AMF along the $\mathbf{a}_H$ direction but to all intents and purposes none along the $\mathbf{b}_H$ direction. The AMF along the $\mathbf{c}_H$ direction is more problematical in that it fluctuates wildly as a function of $\mathbf{q}_H \cdot \mathbf{T}_H$ (modulo an integer) in Fig. 6. One would usually expect modulation amplitudes to decrease monotonically with harmonic order as is the case for all the other AMF's. In this case, however, the modulation amplitude associated with the 12th-order harmonic is almost of the same magnitude as that associated with the second-order harmonic. Our suspicion is that this AMF is implausible but to check this point would require a full refinement using a modulation wave approach. As for the Q sub-structure, it would appear that only two modulation harmonics, again the first and the third, are required to describe the x and y axis AMF's of the H sub-structure. The z axis AMF of the H sub-structure clearly remains to be determined. Again, as for the Q sub-structure, the substantial amplitude of the third-order harmonic of the x axis AMF with respect to the first-order harmonic (see Table 2) gives the corresponding AMF more of a 'square wave' rather than a sinusoidal appearance.

In conclusion, the appropriate superspace-group symmetries characterizing the Q and H sub-structures (and indeed the entire composite-modulated structure depending upon which sub-structure the description is based) in the ZrN_xF_{4-3x} $(0.906 < x < 0.936)$ system have been shown to be P: *Abmm*:1s1̄ for the Q sub-structure and B:*Pmcm*:s1̄1 for the H sub-structure respectively. Fourier decomposition of the previously reported conventional superstructure refinement of one member of this solid-solution field, $Zr_{108}N_{98}F_{138}$, has provided

both underlying parent sub-structures as well as an approximation to the atomic modulation functions (AMF's) describing the mutual influence of the two parent sub-structures upon each other. In addition, this Fourier decomposition has given an indication of the sorts of problems (*e.g.* spurious 'noise' on AMF's) that will inevitably be encountered in accurately determining the appropriate AMF's when a conventional superstructure refinement of such composite modulated structures is attempted. It also
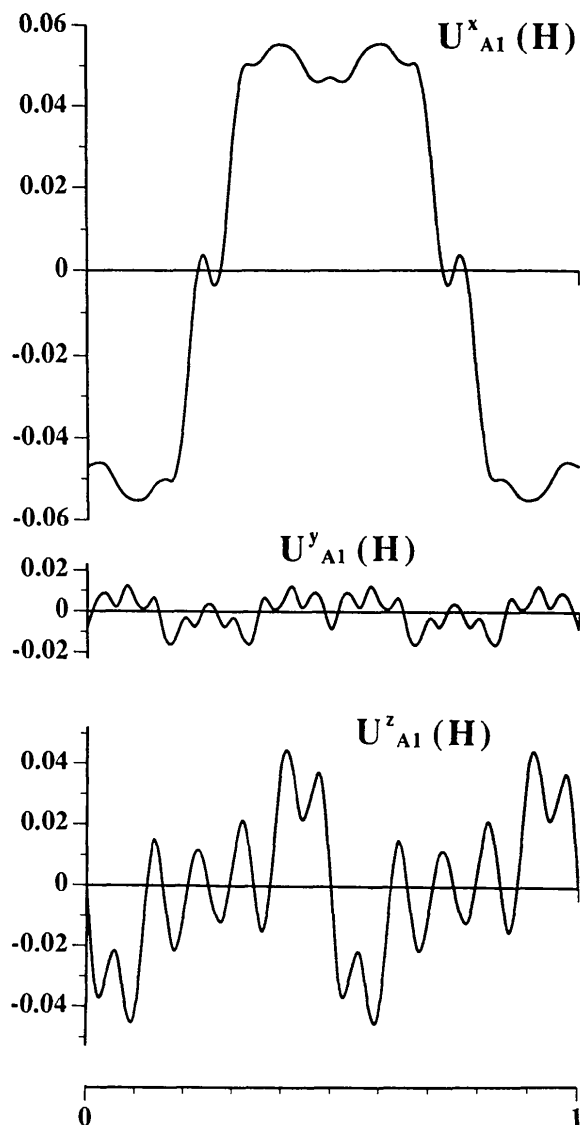

Fig. 7. A plot of the H sub-structure AMF's derived from the Jung & Juza (1973) structure refinement plotted as a function of $\mathbf{q}_H \cdot \mathbf{T}_H$ (modulo an integer). The units of the ordinate axis are fractional coordinates but they have been rescaled so that the height of the appropriate AMF at any particular value of $\mathbf{q}_H \cdot \mathbf{T}_H$ (modulo an integer) is directly proportional to the corresponding shift in Å.

indicates that a full structure refinement based upon a composite modulated structure approach is needed in order to obtain chemically plausible AMF's – in particular the chemically implausible spike associated with the b_Q axis shifts of the Q sub-structure anions and the c_H axis shifts of the H sub-structure should be refined.

References

ABAOUZ, A. (1988). PhD thesis, Univ. of Limoges, France.
BEVAN, D. J. M. & MANN, A. W. (1975). Acta Cryst. B31, 1406–1411.
BEVAN, D. J. M., MOHYLA, J., HOSKINS, B. F. & STEEN, R. J. (1990). Eur. J. Solid State Inorg. Chem. 27, 451–465.
BRADLEY, C. J. & CRACKNELL, A. P. (1972). The Mathematical Theory of Symmetry in Solids. Oxford: Clarendon Press.
HYDE, B. G. & ANDERSSON, S. (1989). Inorganic Crystal Structures. New York: Wiley.
JANNER, A. & JANSSEN, T. (1980). Acta Cryst. A36, 408–415.
JUNG, W. & JUZA, R. (1973). Z. Anorg. Allg. Chem. 399, 129–147.
MAKOVICKY, E. & HYDE, B. G. (1981). Struct. Bonding, 46, 101–176.

MAKOVICKY, E. & HYDE, B. G. (1992). Non-Commensurate Layered Structures, edited by A. MEERSCHAUT, pp. 1–100. Switzerland: Trans Tech Publications.
MANN, A. W. & BEVAN, D. J. M. (1972). J. Solid State Chem. 5, 410–418.
PÉREZ-MATO, J. M. (1991). Methods of Structural Analysis of Modulated Structures and Quasi-crystals, edited by J. M. PÉREZ-MATO, F. J. ZÚÑIGA & G. MADARIAGA, pp. 117–128. Singapore: World Scientific.
PÉREZ-MATO, J. M., MADARIAGA, G., ZÚÑIGA, F. J. & GARCIA ARRIBAS, A. (1987). Acta Cryst. A43, 216–226.
SMAALEN, S. VAN (1989). J. Phys. Conden. Matter, 1, 2791–2800.
SMAALEN, S. VAN (1991a). J. Phys. Conden. Matter, 3, 1247–1263.
SMAALEN, S. VAN (1991b). Phys. Rev. B, 43, 11330–11341.
SMAALEN, S. VAN (1992). Non-Commensurate Layered Structures, edited by A. MEERSCHAUT, pp. 173–222. Switzerland: Trans Tech Publications.
THOMPSON, J. G., WITHERS, R. L., SELLAR, J., BARLOW, P. J. & HYDE, B. G. (1990). J. Solid State Chem. 88, 465–475.
WITHERS, R. L., THOMPSON, J. G. & HYDE, B. G. (1991). Acta Cryst. B47, 166–174.
WOLFF, P. M. DE (1974). Acta Cryst. A30, 777–785.
WOLFF, P. M. DE (1988). Z. Kristallogr. 185, 67.
WOLFF, P. M. DE, JANSSEN, T. & JANNER, A. (1981). Acta Cryst. A37, 625–636.

Two High-Pressure Tungsten Oxide Structures of W3O8 Stoichiometry Deduced from High-Resolution Electron Microscopy Images

BY M. SUNDBERG

Department of Inorganic Chemistry, Arrhenius Laboratory, Stockholm University, S-10691 Stockholm, Sweden

N. D. ZAKHAROV, I. P. ZIBROV, YU. A. BARABANENKOV

Institute of Crystallography, Russian Academy of Sciences, 117333 Moscow, Russia

V. P. FILONENKO

Institute of High Pressure Physics, Russian Academy of Sciences, Troitsk, 149092 Moscow Region, Russia

AND P. WERNER

Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, O-4050 Halle/Saale, Germany

(Received 18 March 1993; accepted 7 June 1993)

Abstract

Two new high-pressure tungsten oxides, prepared at $P = 50 \times 10^5$ kPa and $T = 1773$ K, have been investigated by high-resolution electron microscopy. The formula, W_3O_8 for both phases, and the structures were deduced from the micrographs and verified by simulated image calculations. The phases are both orthorhombic, with the following unit-cell dimensions determined from X-ray powder patterns:

W_3O_8(I), $a = 6.386$ (9), $b = 10.43$ (5), $c = 3.80$ (1) Å, $V = 253.1$ Å^3, $Z = 2$, space group $C222$; W_3O_8(II), $a = 10.35$ (5), $b = 13.99$ (5), $c = 3.78$ (1) Å, $V = 547.3$ Å^3, $Z = 4$, space group $Pbam$. The first structure, W_3O_8(I), which is more dense than the other, is isostructural with U_3O_8 [Andresen (1958). Acta Cryst. 11, 612–614] and with the high-pressure modification of Nb_3O_7F. The less densely packed phase, W_3O_8(II), has a new type of structure, which contains groups of four edge-sharing WO_6 octahedra