research papers

Towards a unified description of the $AMOB_2O_5$ (A = K, Rb, Cs, Tl; M = Nb, Ta) family of compounds

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Single-crystal X-ray diffraction data (Mo $K\alpha$ radiation) are used to re-refine the structure of $RbNbOB_2O_5$, rubidium niobium oxo pyroborate. The structure is refined as an incommensurate modulated structure with superspace group symmetry $Pmn2_1(0,0.4,0)s$ and lattice parameters a = 7.406 (2), b = 3.939 (2) and c = 9.475 (2) Å. Refinement on 3242 unique reflections converged to R = 0.031, while a previous conventional superstructure refinement led to R = 0.090. This lowering of the R factor goes hand-in-hand with a substantial reduction in the number of refined parameters. The refinement strongly suggests that the structure is effectively incommensurately modulated, despite an apparently rational magnitude of the primary modulation wavevector and overlap of satellite reflections.

1. Introduction

Non-centrosymmetric oxo pyroborates, $AMOB_2O_5$ (A = K, Rb, Cs, Tl; M = Nb, Ta; Gasperin, 1974; Baucher & Gasperin, 1975; Baucher *et al.*, 1976; Akella & Keszler, 1995; Becker *et al.*, 1995), have recently attracted considerable interest owing to their potential use as nonlinear optical materials. All members of the family possess a common underlying average structure. In addition, most exhibit superstructures of varying multiplicities (2, 5 and 8) along the *b* axis (corresponding to the $Pmn2_1$ setting of $CsNbOB_2O_5$; Becker *et al.*, 1995). Despite the availability of single crystals for all compounds, single-crystal structure refinements have only been reported for $TlNbOB_2O_5$ (Gasperin, 1974), $RbNbOB_2O_5$ (Baucher *et al.*, 1976), $CsNbOB_2O_5$ (Akella & Keszler, 1995; Becker *et al.*, 1995) and $CsTaOB_2O_5$ (Akella & Keszler, 1995). The Cs compounds are reported without superstructure, *i.e.* to be of the basic structure type, while the Tl compound displays a twofold superstructure and the Rb compound a fivefold superstructure.

An initial electron diffraction investigation of $RbNbOB_2O_5$ (see below) verified the existence of an exact fivefold superlattice along *b*. A characteristic hierarchical intensity distribution among the satellite reflections was strongly suggestive of a modulated structure in that the $\mathbf{G}_p \pm (2/5)\mathbf{b}_p{}^*$ (p represents parent) satellite reflections were clearly much stronger than the $\mathbf{G}_p \pm (1/5)\mathbf{b}_p{}^*$ satellite reflections (see Fig. 1*a*). A re-examination of the reflections used previously to refine the structure of $RbNbOB_2O_5$ (Baucher *et al.*, 1976) confirmed this observation. 1250 observed reflections were used, divided into 781 parent reflections ($k = 5n$) and 469 superstructure reflections ($k \neq 5n$). This is interesting as the number of superstructure reflections should theoretically be much larger (up to four times larger) than the number of parent reflections.

However, even more interesting is the fact that amongst the superstructure reflections hardly any reflections with $k = 5n \pm 1$, *i.e.* satellite reflections of the form $\mathbf{G}_p \pm (1/5)\mathbf{b}_p{}^*$, are observed (only 17 in total). Such a lack of higher-order harmonic satellite reflections suggests that $RbNbOB_2O_5$ is effectively incommensurately modulated (Pérez-Mato, 1991), despite the existence of an exact fivefold superlattice along **b**.

On other occasions such facts have been highly indicative of the need for, and advantage of, a modulation wave approach to structure refinement. This is further supported by the existence of a complete solid solution in the system $TlNb_xTa_{1-x}OB_2O_5$, $0 \leq x \leq 1$ (Baucher & Gasperin, 1975), and the recent discovery of complete solid solutions in the Rb/K and Rb/Cs niobium oxo pyroborates (Akella & Keszler, 1995). A modulation wave approach potentially allows for a unified view of the structures, crystal chemistry and optical

Figure 1
(*a*) ⟨201⟩ and (*b*) [100] zone-axis electron diffraction patterns (EDPs) characteristic of RbNbOB$_2$O$_5$. Indexation is with respect to basis vectors $\mathbf{a}_p{}^*$, $\mathbf{b}_p{}^*$, $\mathbf{c}_p{}^*$ and $\mathbf{q}$ [= $(2/5)\mathbf{b}_p{}^*$], respectively.

properties of this family of materials (Withers *et al.*, 1998). Re-refinement of RbNbOB$_2$O$_5$ (Baucher *et al.*, 1976) as a modulated structure is found to lead to an improved crystal chemistry and lower R values, while at the same time significantly reducing the number of refinable parameters.

2. Electron diffraction/symmetry considerations

Fig. 1 shows (*a*) ⟨201⟩ and (*b*) [100] zone-axis electron diffraction patterns (EDP's) characteristic of RbNbOB$_2$O$_5$. Indexation is with respect to basis vectors $\mathbf{a}_p{}^*$, $\mathbf{b}_p{}^*$, $\mathbf{c}_p{}^*$ and $\mathbf{q}$ [= $(2/5)\mathbf{b}_p{}^*$], respectively. The primary modulation wavevector (see, for example, Pérez-Mato *et al.*, 1987) has been chosen to be $(2/5)\mathbf{b}_p{}^*$ rather than $(1/5)\mathbf{b}_p{}^*$, because the $\mathbf{G}_p \pm (2/5)\mathbf{b}_p{}^*$ satellite reflections are invariably much stronger than the barely visible second-order harmonic $\mathbf{G}_p \pm (1/5)\mathbf{b}_p{}^*$ satellite reflections whenever $\mathbf{b}_p{}^*$ is excited, as is apparent from Fig. 1(*a*). The one exception to this rule is at the [100] zone-axis orientation of Fig. 1(*b*), where the second-order harmonic $\mathbf{G}_p \pm (1/5)\mathbf{b}_p{}^*$ satellite reflections are still barely visible, but where the primary $\mathbf{G}_p \pm (2/5)\mathbf{b}_p{}^*$ satellite reflections are systematically absent. Such an 'extinction condition' [*i.e.* $F(0klm) = 0$ unless m is even] cannot be explained from a conventional superstructure point of view and provided the initial motivation for using a modulation wave, rather than the superstructure, approach to structure refinement. From an irreducible representation or superspace point of view, such an extinction condition implies the existence of a superspace symmetry operator of the form $\{-x_1, x_2, x_3, x_4 + \frac{1}{2}\}$ (van Smaalen, 1995).

Fig. 2 shows a wide-angle view of an [010] zone-axis EDP of RbNbOB$_2$O$_5$, including the first superlattice Higher-Order Laue Zone (HOLZ) ring at $(1/5)\mathbf{b}_p{}^*$. The first reflection along the vertical direction in the Zero OLZ (ZOLZ) portion of the EDP is $2\mathbf{a}_p{}^*$, while the first reflection along the horizontal direction is $2\mathbf{c}_p{}^*$. Note the characteristic azimuthal intensity variation of the first superlattice HOLZ ring at $(1/5)\mathbf{b}_p{}^*$ with the strongest satellite reflections occurring parallel to the $\mathbf{a}_p{}^*$ direction of reciprocal space and implying that the atomic shifts responsible must be largely polarized along the $\mathbf{a}_p$ direction of real space. A further feature is the characteristic extinction condition [$F(h0l0) = 0$ unless $h + l$ is even] apparent in the ZOLZ region of the EDP. Such an extinction condition implies the existence of a superspace symmetry operator of the form $\{x_1 + \frac{1}{2}, -x_2, x_3 + \frac{1}{2}, -x_4 + 2\delta\}$. Taken together with the $\{-x_1, x_2, x_3, x_4 + \frac{1}{2}\}$ symmetry operator required by the extinction condition apparent in Fig. 1(*b*), the implied overall superspace group symmetry is thus $Pmn2_1(0,0.4,0)s$ (Jansen *et al.*, 1992).

For a truly incommensurately modulated structure, the parameter δ can be freely chosen. For a commensurately modulated structure, as in the current case where $\mathbf{q}$ apparently equals $(2/5)\mathbf{b}^*$ exactly, the choice of the global phase parameter δ determines the resultant conventional three-dimensional space-group symmetry (van Smaalen, 1995; Pérez-Mato, 1991; Yamamoto & Nakazawa, 1982; Wiegers *et al.*, 1990). The possible three-dimensional supercell space-group symmetries
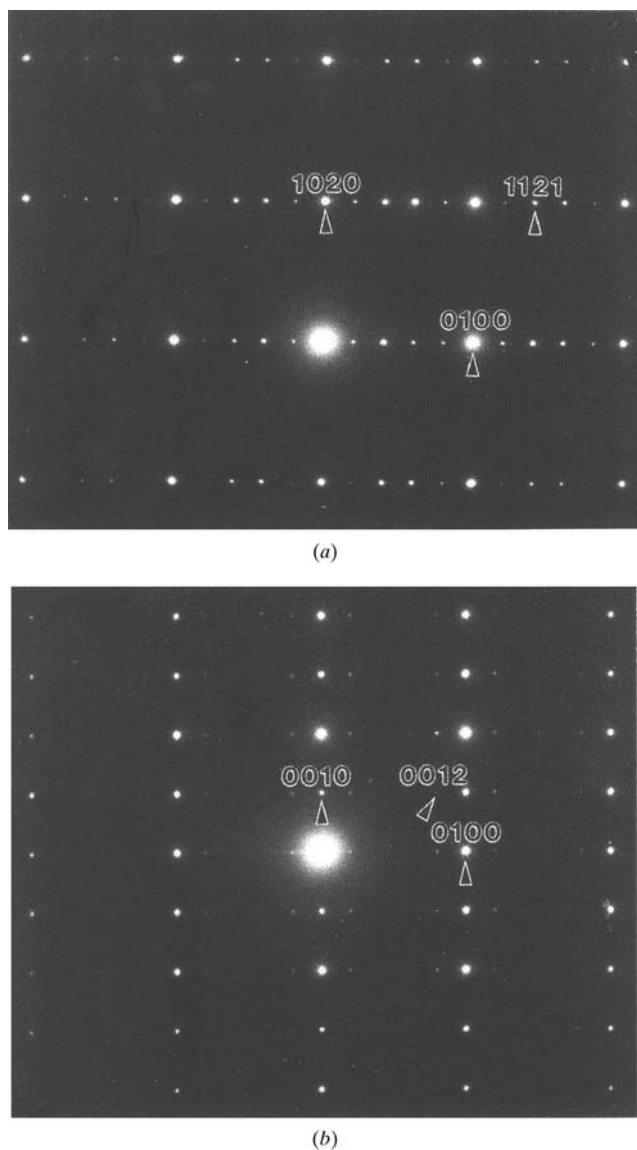
Table 1
Important parameters.

Formula	$RbNbOB_2O_5$
Space group	$Pmn2_1(0,0.4,0)s$
a (Å)	7.406 (2)
b (Å)	3.939 (2)
c (Å)	9.475 (2)
Volume (Å^3)	276.4
Formula weight	296.0
Z	2
Density (g cm^{-3})	3.556
Wavelength (Å)	0.71073 (Mo $K\alpha$)
Monochromator	Graphite
Scan mode	$\omega/2\theta$ scans
Scan width (° in ω)	$1.0 + 0.35\tan\theta$
Scan speed (° min^{-1})	2
Attenuation factor	16.04
μ (mm^{-1})	10.88
θ range (°)	1.5–33
h,k,l,m range	$\pm11, \pm6, \pm14, \pm2$
Reflections measured	20 071
Reflections [$I > 3\sigma(I)$]	10 153
Reflections unique	5293
Reflections unique [$I > 3\sigma(I)$]	3242
R_{int} [$I > 3\sigma(I)$/all]	0.0313/0.0364
Absorption correction	Gaussian (14 × 14 × 14 grid)
Extinction correction	Isotropic, type II, 4.04 (3)

of $RbNbOB_2O_5$ are given by $P1n1$ (for $\delta = 2n/20$, with n being an integer), $P112_1$ [for $\delta = (2n + 1)/20$] and $P1$ (otherwise). All previous superstructure refinements of $RbNbOB_2O_5$ have assumed the resultant $P1n1$ space-group symmetry.

3. Experimental

3.1. Synthesis

A mixture of Rb_2CO_3, Nb_2O_5 and B_2O_3 in the required stoichiometry was ground together and then heated in a sealed platinum tube. The platinum tube was heated at a rate of 200 K h^{-1}, held at 1373 K for 1 d and then slowly cooled to room temperature at a rate of 10 K h^{-1}. Soaking the reaction mixture in water allowed the isolation of single crystals of $RbNbOB_2O_5$. The crystal used for data collection was a clear, colourless plate with approximate dimensions $0.2 \times 0.1 \times 0.05$ mm^3.

3.2. Intensity measurement and data processing

Accurate lattice parameters (see Table 1) were obtained from a least-squares fit of the setting angles for 25 reflections with 2θ values between 23 and 33° for Mo $K\alpha$ radiation.[1] For data collection a Philips PW1100/20 diffractometer was used. Background counting time was 7 s on either side of the scan. Square slits subtended angles of $1 \times 1°$ at the crystal.

The setting for this structure refinement has been changed with respect to the original setting of Baucher *et al.* (1976) in order to be compatible with the standard setting of the *International Tables for Crystallography* (Hahn, 1995) and most other published structures in this family of compounds,

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[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR0089). Services for accessing these data are described at the back of the journal.

i.e. **b** now represents the modulation direction. The data collection was performed for a five-times superstructure along **b** on a Philips PW1100/20 diffractometer (Grigg & Barnea, 1993).

Lorentz–polarization and absorption corrections were performed using the program package *Xtal*3.4 (Hall *et al.*, 1995). The three standard reflections measured every 180 min showed no significant change in intensity. Averaging the reflection intensities in Laue symmetry *mm2* gave 5293 unique reflections ($R_{int} = 0.031$). Other important parameters for the data collection are given in Table 1.

4. Refinement details

The modulated structure refinements were carried out using the software package *JANA*98 (Petříček & Dušek, 1998). Scattering factors for neutral atoms were taken from *International Tables for Crystallography* (Wilson, 1992). Refinement using full-matrix least-squares was on F employing unit weights, which increases the significance of relatively weak satellite reflections. Atoms were refined with anisotropic atomic displacement parameters.

The magnitude of the primary modulation wavevector appears to be $0.4b^*$ exactly. Therefore, it is difficult to establish whether modulation waves of higher order than two genuinely exist, as the corresponding higher-order harmonic satellite reflections will necessarily coincide with first- and second-order satellite reflections or parent reflections. Reflections are always assigned the lowest possible satellite index, *i.e.* no satellite reflections with $|m| > 2$ are in the data set. If there are modulation waves of higher order than 2 with significant
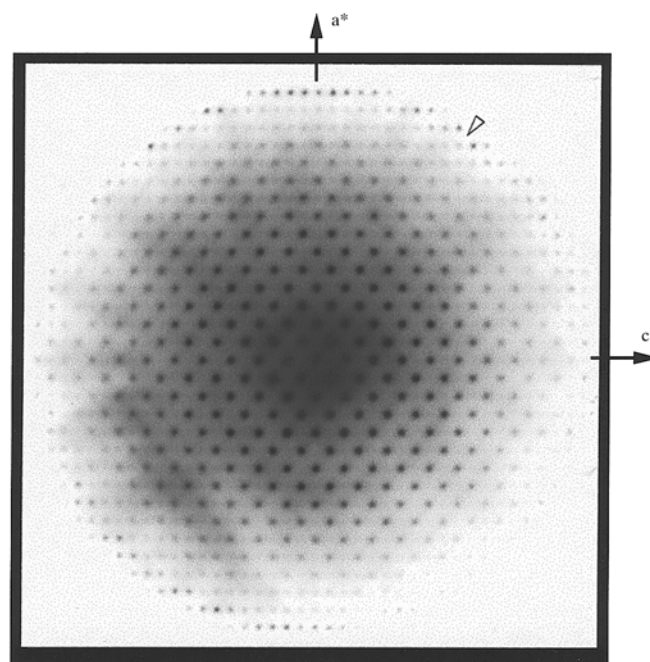

Figure 2
A wide angle view of an [010] zone-axis EDP of $RbNbOB_2O_5$, including the first superlattice Higher-Order Laue Zone (HOLZ) ring at $(1/5)\mathbf{b}_p^*$.

amplitude the phase relationship between overlapping reflections needs to be determined (Schmid *et al.*, 1997).

As the primary modulation wavevector runs along **b***, the little co-group (Bradley & Cracknell, 1972) of each modulation harmonic is thus $\{E, m_x\}$ with two corresponding irreducible representations, one with a character of -1 under $\{m_x|\mathbf{0}\}$ and the other with a character of $+1$ under $\{m_x|\mathbf{0}\}$. A superspace symmetry of $Pmn2_1(0,0.4,0)s$ implies that odd-order harmonics transform according to the first of these irreducible representations, while even-order harmonics transform according to the second. The structure-factor contributions arising from overlapping even- and odd-order harmonics [such as, for example, overlapping second- and third-order harmonics or overlapping first- and fourth-order harmonics for $\mathbf{q} = (2/5)\mathbf{b}^*$] are thus mutually orthogonal and their overlap does not result in a locking-in of the overall global phase. This latter requires overlapping contributions belonging to the same irreducible representation and implies that up to fifth-order harmonics ought to have significant amplitude if the 'incommensurate' modulation is to be genuinely considered to be locked in. Given the weakness of the observed second-/third-order harmonic satellite reflections at $\mathbf{G} \pm (1/5)\mathbf{b}^*$ in conjunction with the apparent validity of the condition $F(0klm) = 0$ unless m is even (see Fig. 1*b*), this seems highly unlikely.

This question of the number of modulation harmonics with significant amplitude has implications for the various refinement strategies. If one assumes that the structure is incommensurately modulated, then only up to second-order coefficients can be refined reasonably owing to the unique indexation assumption underpinning the incommensurate structure refinement. There are formally no reflections in the data set with $|m| > 2$ (see above), therefore, there are no observations against which to refine any coefficients higher than second order. For an incommensurate refinement which allows overlap of reflections $hklm$ and $h, k + 2, l, m - 5$, this restriction is not applicable and higher-order coefficients can justifiably be added.

A refinement as a commensurate modulated structure bears even more complications. As shown in Section 2, depending on the choice of global phase there are three different possible resultant space groups. They are all subgroups of $Pmn2_1$ and therefore there are formally more independent reflections and lower site symmetries. Releasing all these additional degrees of freedom simultaneously invariably leads to correlations between parameters as there is not enough information in the data set to justify lowering of the point-group symmetry from the higher $mm2$ point-group symmetry. The only reasonable way to proceed therefore is to use a commensurate modulation wave approach, *i.e.* consider all possible contributions to any one structure factor, whilst maintaining the same parameter constraints as they were in the higher symmetry space group.

The structure was initially refined as an incommensurate modulated structure. The starting model for the refinement of the structure (*i.e.* average positions) was taken from the previously published structure of RbNbOB$_2$O$_5$ (Baucher *et al.*,

(*a*)

(*b*)
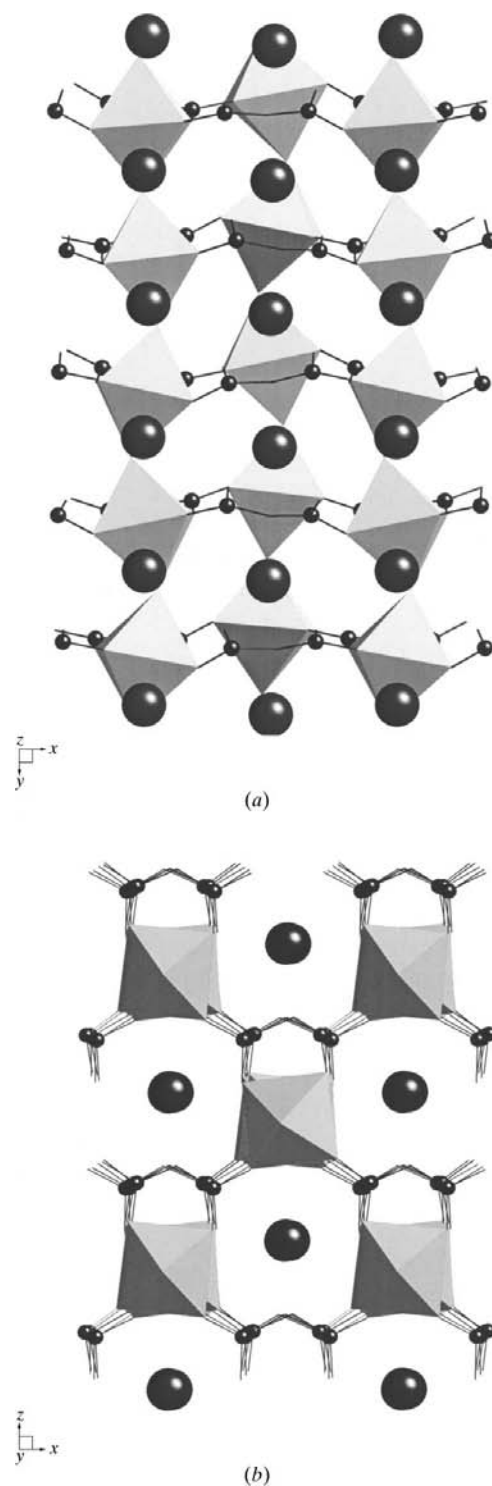
Figure 3
(*a*) Part of the RbNbOB$_2$O$_5$ structure in projection along **c** (**b** down the page, **a** to the right). The niobium oxygen octahedra are rotated relative to **c** [large spheres: Rb; small spheres: B; Nb at the centre of the octahedra, O at the corners of the octahedra (O1 and O2 in the basal plane, O4 at the apices) and between the B atoms (O3)]. (*b*) Projection along **b** (**c** up the page, **a** to the right). The niobium oxygen octahedra are slightly rotated relative to **b** [large spheres: Rb; small spheres: B; Nb at the centre of the octahedra, O at the corners of the octahedra (O1 and O2 in the basal plane, O4 at the apices) and between the B atoms (O3)].

Table 2
R values for comparative refinements.

Note: Superstructure refinement in *Pn* (Baucher *et al.*, 1976) has 50 independent atoms which corresponds to 148 refineable displacive parameters. Modulated structure refines 34 thermal parameters + 2 (scale and extinction).

	δ	No. of parameters	R(overall)	R(parent)	R(first order)	R(second order)
Model 1	0	78	0.0553	0.0216	0.0597	0.4384
Model 2	0	112	0.0407	0.0193	0.0570	0.2264
Model 3	0	138	0.0313	0.0189	0.0484	0.1068
Model 4	0	172	0.0307	0.0190	0.0464	0.1050
Model 5	0	138	0.0384	0.0198	0.0590	0.1740
Model 6	0	172	0.0383	0.0197	0.0589	0.1728
Model 7	0	184	0.0381	0.0195	0.0587	0.1730
Model 8	0.25	184	0.0389	0.0204	0.0578	0.1786
Model 9	0.025	184	0.0386	0.0197	0.0585	0.1804

Table 3
Fractional coordinates of the average structure.

	x	y	z
Rb	1/2	0.96264 (9)	0.098378
Nb	0	0.33073 (5)	0.99583(4)
B	0.8348 (3)	0.5181 (7)	0.2834 (2)
O1	0.8196 (2)	0.3984 (6)	0.1507 (2)
O2	0.6883 (3)	0.6178 (6)	0.3560 (2)
O3	0	0.5492 (8)	0.3507 (3)
O4	1/2	0.1143 (6)	0.4953 (4)

1976). In the first step only the average structure was refined using parent reflections exclusively. Then the first-order displacive modulation wave amplitudes for each of the atoms were added step-by-step and refined from a starting value of ±0.0001 using all reflections. All possible sign combinations for these modulation wave amplitudes were tested in the refinement. The correct combination of signs resulted in significantly lower *R* values than any of the other possibilities (Table 2, Model 1; note: the signs of all first-order coefficients can be reversed without changing the *R* values). The second-order coefficients were then released for refinement with ±0.0001 as the starting values. False minima were investigated by systematically reversing the sign of various modulation wave amplitudes at the completion of the structure refinement (see Table 2, Model 2). Then third-order coefficients were included and it was shown that while this improved the *R* values, only by allowing for overlap was it possible to refine magnitudes that seemed sensible and achieve even lower *R*

values (see above; Table 2, Model 3). Adding fourth-order coefficients and allowing for overlap did not significantly lower the *R* values (Table 2, Model 4) and was therefore not considered instructive.

The refinement as a commensurately modulated structure was carried out starting from the parameters of Model 3, but assuming a commensurate modulation. This was performed for a choice of δ values to investigate the dependence of the refinement statistics on the global phase. Up to fifth-order satellites were added for any value of δ and the final *R* values given in Table 2, Models 5–9. It can be seen that despite the increased number of parameters (Models 7–9 refine the maximum number of displacive parameters, *i.e.* the same number as for a superstructure refinement), the *R* values have not improved and furthermore the *R* values are almost independent of the value of δ. This demonstrates that the global phase parameter δ is not a refinable quantity, *i.e.* despite the apparent overlap of reflections the structure is effectively incommensurately modulated.

In the incommensurate refinement, allowing for overlap (see above), the lowest-order structure-factor contributions, $A(hklm)$, $B(h, k + 2, l, m - 5)$ and $C(h, k + 4, l, m - 10)$ say, are automatically presumed to be orthogonal to each other so that
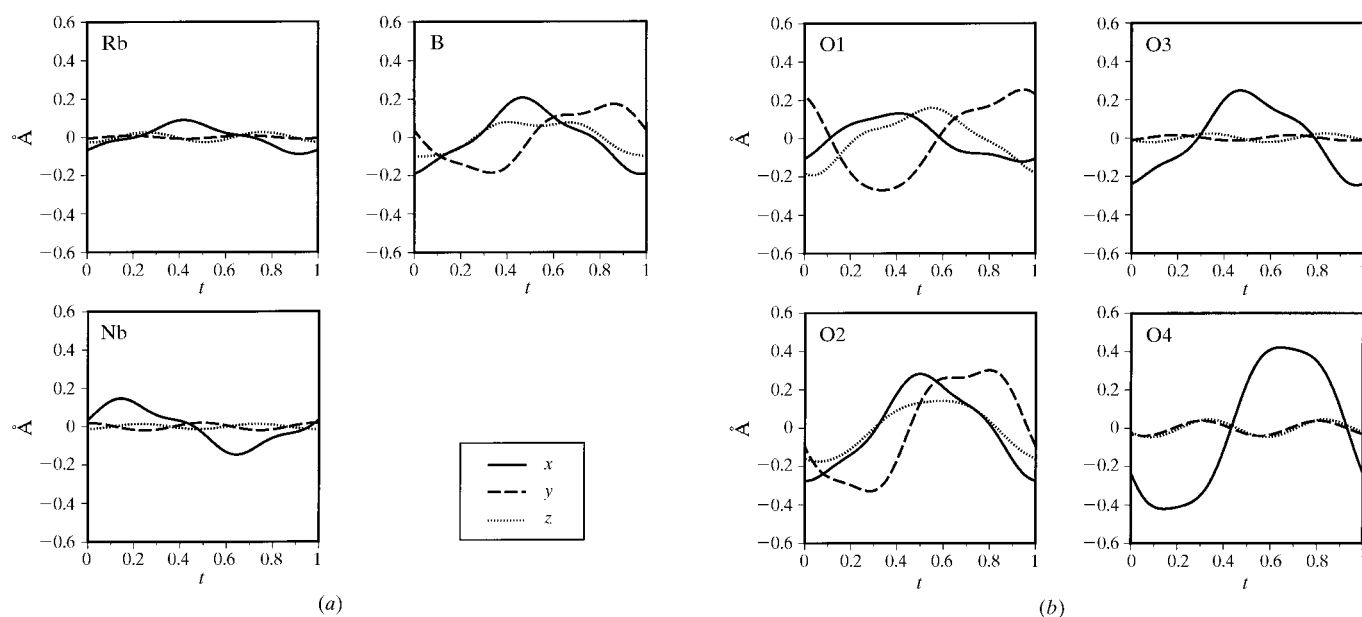

Figure 4
(*a*) Final refined metal AMFs U_M^x, U_M^y and U_M^z plotted in absolute coordinates as a function of $t = (\mathbf{q}.\mathbf{T} - \delta)$ modulo an integer. (*b*) Final refined oxygen AMFs U_O^x, U_O^y and U_O^z plotted in absolute coordinates as a function of $t = (\mathbf{q}.\mathbf{T} - \delta)$ modulo an integer.

Table 4
Displacive Fourier terms (in fractional coordinates).

	Rb	Nb	B	O1	O2	O3	O4
$x\sin 1$	−0.00921 (7)	0.01562 (4)	−0.0225 (5)	−0.0026 (3)	−0.0340 (4)	−0.0303 (5)	−0.0612 (5)
$y\sin 1$	0	0	−0.004 (1)	0.0067 (9)	−0.019 (1)	0	0
$z\sin 1$	0	0	−0.0100 (4)	−0.0143 (3)	−0.0157 (3)	0	0
$x\cos 1$	0.00412 (7)	−0.00575 (4)	−0.0071 (5)	−0.0164 (3)	0.0084 (4)	−0.0032 (5)	−0.0097 (6)
$y\cos 1$	0	0	0.045 (1)	0.0646 (8)	0.0825 (8)	0	0
$z\cos 1$	0	0	−0.0005 (4)	−0.0068 (3)	0.0066 (3)	0	0
$x\sin 2$	0	0	0.0011 (6)	−0.0002 (4)	0.0009 (5)	0	0
$y\sin 2$	0.0016 (3)	0.0050 (1)	0.001 (1)	0.007 (1)	0.001 (1)	−0.003 (2)	−0.010 (1)
$z\sin 2$	0.0027 (1)	−0.00138 (9)	−0.0002 (5)	−0.0019 (4)	0.0010 (4)	0.0015 (5)	−0.0047 (7)
$x\cos 2$	0	0	0.0001 (6)	0.0016 (4)	−0.0005 (4)	0	0
$y\cos 2$	0.0014 (3)	−0.0002 (2)	−0.004 (2)	−0.010 (1)	−0.004 (1)	0.001 (2)	−0.002 (1)
$z\cos 2$	−0.0007 (1)	−0.00025 (8)	0.0021 (6)	0.0008 (4)	0.0015 (4)	0.0019 (7)	0.0002 (8)
$x\sin 3$	0.0013 (2)	−0.00365 (8)	−0.000 (1)	−0.0013 (7)	0.0034 (6)	−0.0008 (9)	−0.0058 (8)
$y\sin 3$	0	0	0.007 (3)	0.002 (2)	0.012 (2)	0	0
$z\sin 3$	0	0	−0.002 (1)	0.0021 (7)	−0.0002 (6)	0	0
$x\cos 3$	−0.0017 (2)	0.0007 (1)	0.0039 (9)	0.0022 (7)	0.0027 (6)	0.0047 (9)	−0.0013 (7)
$y\cos 3$	0	0	−0.003 (3)	−0.006 (2)	−0.005 (2)	0	0
$z\cos 3$	0	0	−0.000 (1)	0.0017 (7)	0.0005 (7)	0	0

Table 5
Atomic displacement parameters (Å^2).

	Rb	Nb	B	O1	O2	O3	O4
U^{11}	0.0241 (2)	0.00793 (8)	0.0117 (9)	0.0103 (6)	0.0131 (8)	0.012 (1)	0.022 (1)
U^{22}	0.0240 (2)	0.00974 (9)	0.017 (1)	0.029 (1)	0.028 (1)	0.037 (1)	0.0149 (8)
U^{33}	0.0247 (1)	0.00794 (8)	0.0101 (8)	0.0108 (7)	0.0142 (7)	0.0137 (9)	0.025 (1)
U^{12}	0	0	0.0004 (8)	−0.0015 (7)	0.0013 (7)	0	0
U^{13}	0	0	0.0030 (7)	0.0020 (5)	0.0049 (6)	0	0
U^{23}	0.0038 (1)	−0.0003 (9)	−0.0002 (8)	−0.0050 (8)	−0.0008 (8)	−0.0057 (9)	−0.004 (1)

the calculated intensity $I = |A|^2 + |B|^2 + |C|^2$. In the case of the commensurate modulated structure refinements, the relative phase of the structure-factor contributions separated by 10 in harmonic order is dependent upon the choice of global phase δ. If $|C| \neq 0$, then the refinement statistics ought to be dependent upon the choice made for δ. This, however, is not the case.

In summary, the structure of $RbNbOB_2O_5$ is best refined and described as an incommensurate modulated structure (with overlap), despite the apparent exact five-times super-structure that is formed by that compound. The final refinement converged to an overall R value of 0.031 ($wR = 0.035$) once an isotropic extinction correction had been incorporated (see Tables 1 and 2). Final refined parameters for the average substructure and displacive modulation wave amplitudes are given in Tables 3 and 4, respectively. Atomic displacement parameters are given in Table 5. This final refinement forms the basis for the following section.

5. Results and discussion

5.1. Structure

Fig. 3(a) shows a projection of the structure down **c**. For ease of comparison with Baucher *et al.* (1976) one 'supercell' along **b** [$5b_p = c$ (Baucher *et al.*, 1976)] is shown. This origin corresponds to $\delta = 0$, resulting in a 'supercell' space-group symmetry of $P1n1$. It is readily seen that the niobium oxygen

octahedra are strongly displaced from the average position along the *a* direction, resulting in a rotation of the octahedra around **c**. The boron ions are mainly displaced along the *b* direction. The projection down **b** in Fig. 3(b) shows a slight rotation of the niobium oxygen octahedra with respect to the *b* axis and small displacements of the boron ions.

5.2. Atomic modulation functions

The refined displacive atomic modulation functions (AMFs) for the final model as a function of $t = (\mathbf{q}.\mathbf{T} - \delta)$ modulo an integer are shown in Figs. 4(a) and (b). Note that Rb, Nb, O3 and O4 occupy 2(a) sites (m..) and O1, O2 and B occupy general sites in the structure. Rb, Nb and B display only relatively small modulation amplitudes (< 0.1 Å for Rb, and < 0.2 Å for B and Nb). For the oxygen ions, only x(O4), x(O3), x(O2) and y(O2) show modulation amplitudes > 0.2 Å, with x(O4) being the largest at ~0.45 Å.

Fig. 5 shows the variation in the coordination sphere of Rb as a function of $t = (\mathbf{q}.\mathbf{T} - \delta)$ modulo an integer. Rb is coor-

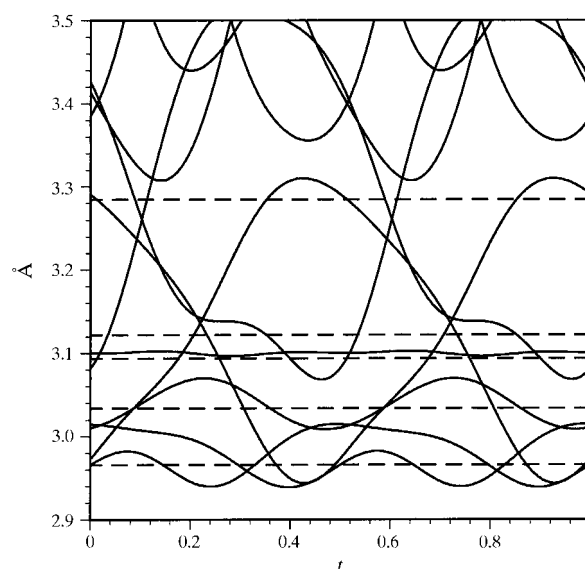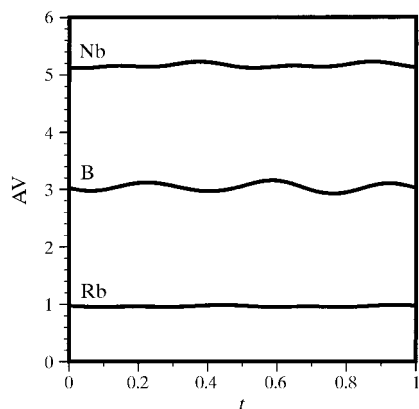**Figure 5**
The variation in the coordination sphere of Rb as a function of $t = (\mathbf{q}.\mathbf{T} - \delta)$ modulo an integer. The dashed lines show the distance variation in the average structure (Note: lines at 2.965, 3.122 and 3.285 Å have a multiplicity of 2).

Figure 6
The variation for the apparent valences of Rb, Nb and B as a function of $t = (\mathbf{q}.\mathbf{T} - \delta)$ modulo an integer. It is readily seen that there is only an insignificant variation around the ideal values of 1, 5 and 3, respectively.

dinated by seven to eight oxygen ions ($d_{max} < 3.3$ Å), depending on the value of $\mathbf{t}$. The coordination sphere of Rb is chosen here, because it shows the largest variation in bond distances if compared with Nb and B.

5.3. Apparent valence calculations

Apparent valences (AVs; Brown & Altermatt, 1985; O'Keeffe, 1989) are often an extremely useful guide to the reliability of refined crystal structures. AVs were calculated for all atoms in the modulated structure using *GRAPHT* within the *JANA*98 package (Fig. 6; Petříček & Dušek, 1998). $R_{ij}^0(\mathrm{Rb}^{1+}-\mathrm{O}^{2-}) = 2.26$, $R_{ij}^0(\mathrm{Nb}^{5+}-\mathrm{O}^{2-}) = 1.911$ and $R_{ij}^0(\mathrm{B}^{3+}-\mathrm{O}^{2-}) = 1.371$ Å (Brese & O'Keeffe, 1991) were used. The resulting AVs confirm the plausibility of the crystal chemistry of the structure. The mean AV for the Rb sites is around 1.0 ± 0.1, for Nb around 5.1 ± 0.1, for B around 3.0 ± 0.1 and for the O atoms one finds approximately 2.0 ± 0.1. For the super-structure refinement of RbNbOB$_2$O$_5$ (Baucher *et al.*, 1976) less consistent values are found, *i.e.* Rb ranges from 0.9 to 1.0, Nb from 4.8 to 5.6, B from 2.7 to 3.4 and O from 1.8 to 2.3. It is readily seen that the spread of values that existed in the superstructure refinement has virtually disappeared. This again highlights the advantage of a modulated structure approach which constrains the atoms to move in a sensible fashion, taking into account the information contained in reciprocal space.

6. Conclusions

A modulated structure approach has been used to re-refine and describe the structure of RbNbOB$_2$O$_5$. Starting values for the displacive modulation wave amplitudes used in the refinement were derived from a previously reported super-structure refinement. Refinement in terms of modulation waves proved to be very stable and resulted in an improved crystal chemistry. The overall R value for the modulated structure refinement is substantially lower than for the superstructure refinement (0.031 compared with 0.090), while employing a vastly reduced number of positional parameters. It is expected that these refinement results will be successfully transferred to the structure of KNbOB$_2$O$_5$, which adopts an eightfold superstructure and has not been refined to date.

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