

analysis. The first is to apply the three-dimensional symmetry for basic or average structure and to develop a model SFF, usually simplified, based on extra periodic parameters, without definite solution of the symmetry problems [eventually reducing the problem to that of the superstructure, see *e.g.* Böhm (1975), Shiozaki (1971) and Schulz (1974)]. The second approach is based on the development of the $(3+d)$ -dimensional space-group theory (Yamamoto, 1983). This makes it possible to refine the modulated structure in an analogous way to that of normal structure, but at the cost of a more complicated form of SFF, which requires numerical integration. In addition, one has to face ambiguity when dealing with the temperature factors. The present study shows that the $(3+1)$ -dimensional symmetry approach to the structure refinement can be simplified in many cases important in practice.

The analytical form of the SFF has been presented for harmonic approximation with arbitrarily oriented amplitudes (*e.g.* elliptic waves), small displacive amplitudes, the corresponding mixed displacive and occupational modulations and for the temperature factors in a new form able to describe the thermal vibrations in the case of elliptic displacive harmonic waves. The temperature-factor corrections obtained are in keeping with corrections by Axe based on physical assumptions. We have shown that these corrections correspond to the zero- and second-order

temperature-factor harmonics among those introduced by Yamamoto.

The results of this paper have been used to prepare a set of least-squares-refinement-type programs to refine the modulated structures. These programs have been successfully applied in the refinement of the modulated phase of NaNO_2 .

The authors are greatly indebted to Professor K. Łukasiewicz for stimulating discussion and valuable comments.

References

- AALST, W. VAN, DEN HOLLANDER, J., PETERSE, W. J. A. M. & DE WOLFF, P. M. (1976). *Acta Cryst.* **B32**, 47–58.
 ADLHART, W. (1982). *Acta Cryst.* **A38**, 498–504.
 AXE, J. D. (1980). *Phys. Rev. B*, **21**, 4181–4190.
 BÖHM, H. (1975). *Acta Cryst.* **A31**, 622–628.
 KOPTSIK, V. (1978). *Ferroelectrics*, **21**, 499–501.
 LITVIN, D. B. (1980). *Phys. Rev. B*, **21**, 3184–3192.
 OVERHAUSER, A. W. (1971). *Phys. Rev. B*, **3**, 3173–3182.
 ROLLET, J. S. (1965). *Computing Methods in Crystallography*. Oxford: Pergamon Press.
 SCHULZ, H. (1974). *Acta Cryst.* **B30**, 1318–1332.
 SHIOZAKI, Y. (1971). *Ferroelectrics*, **2**, 245–254.
 STEURER, W. & ADLHART, W. (1983). *Acta Cryst.* **B39**, 349–355.
 WOLFF, P. M. DE, JANSSEN, T. & JANNER, A. (1981). *Acta Cryst.* **A37**, 625–636.
 YAMAMOTO, A. (1982a). *Acta Cryst.* **A38**, 87–92.
 YAMAMOTO, A. (1982b). *Acta Cryst.* **B38**, 1446–1451.
 YAMAMOTO, A. (1982c). *Acta Cryst.* **B38**, 1451–1456.
 YAMAMOTO, A. (1983). *Acta Cryst.* **B39**, 17–20.

Acta Cryst. (1985). **A41**, 466–469

Refinement of the Incommensurate Crystal Structure of NaNO_2 in $(3+1)$ -Dimensional Space Groups

BY D. KUCHARCZYK AND W. A. PACIOREK

Institute for Low Temperature and Structure Research, Polish Academy of Sciences, pl. Katedralny 1, 50-950 Wrocław, Poland

(Received 8 October 1984; accepted 15 April 1985)

Abstract

Two basic models of the incommensurate (IC) structure of NaNO_2 , one with purely occupational modulation and one with mixed modulation, have been tested using $(3+1)$ -dimensional space groups. The refinements were performed in the two superspace groups $P_{1s}^{1m}m$ and $P_{ss}^{12m}m$. The main feature of this IC structure is the presence of the weak displacive waves superposed on the main modulating waves of the occupational type. The displacements of atoms take place only along the b axis. The amplitude of the displacive wave of the Na^+ ion was found to be almost twice as large (0.077 \AA) as that of the NO_2^-

molecule (0.042 \AA) with the occupational amplitudes approximately the same. The best refinement yields an overall R factor of 0.063 in the $P_{ss}^{12m}m$ group, revealing a small phase shift between individual waves of the Na^+ ion and the NO_2^- molecule. There are, however, practically no phase shifts between the two kinds of modulation waves involved. All waves were found to be harmonic.

Introduction

The structure of the antiferroelectric (AF) phase of NaNO_2 was refined by Kucharczyk, Pietraszko &

Table 1. Restrictions on possible modulating parameters for the chosen space groups

Forbidden parameters are marked with *.

Space group	Position	$u_x^{\mu,c}$	$u_x^{\mu,s}$	$u_y^{\mu,c}$	$u_y^{\mu,s}$	$u_z^{\mu,c}$	$u_z^{\mu,s}$	p_c^μ	p_s^μ
$P_{1\ s\ 1}^{I\ m\ m\ m}$	0, y, 0	*			*	*	*		*
	0, y, z	*			*	*	*		*
$P_{s\ s\ 1}^{I\ 2\ m\ m}$	0, y, 0				*	*			
	0, y, z				*	*			

Lukaszewicz (1978) for a mixed occupational and displacive modulation model. This model was later supported by theoretical studies (Ehrhardt & Michel, 1981; Michel, 1981; Heine & McConnell, 1984; McConnell & Heine, 1984; Heine, Lynden-Bell, McConnell & McDonald, 1985). However, owing to a number of simplifications concerning the symmetry treatment, the refinement procedure and some arbitrariness in the phase relationship between the modulating waves, the structure obtained is no longer a good base for more detailed studies. The decision was taken, therefore, to reinvestigate this structure by applying the recently developed approach to modulated structure determination.

A set of special least-squares refinement programs has been written by one of us (WAP) according to the structure-factor formulas obtained and presented in the preceding paper (Paciorek & Kucharczyk, 1985).

Two basic models, one with purely occupational modulation and one with mixed modulation waves, have been tested using (3+1)-dimensional space groups [according to the de Wolff, Janssen & Janner (1981) notation].

In view of recent works by Ehrhardt & Michel (1981) and Michel (1981) the behaviour of the Na^+ and NO_2^- ions is expected to be different. Thus the individual modulating waves are allowed in the refinement, contrary to our first attempt (Kucharczyk *et al.*, 1978).

Symmetry and refinement procedure

The symmetry of the AF phase of NaNO_2 has been determined by Janner & Janssen (1980). The authors proposed the $P_{1\ s\ 1}^{I\ m\ m\ m}$ space group based on a model of AF structure by Böhm (1977) and the well known symmetry of para- and ferroelectric phases. This group has the following elements:

$$(0, 0, 0, 0); (1/2, 1/2, 1/2, 0) +$$

$$x, y, z, t; \bar{x}, y, z, \bar{t}; x, y, \bar{z}, t; x, \bar{y}, z, t + 1/2;$$

$$x, \bar{y}, \bar{z}, t + 1/2; \bar{x}, y, \bar{z}, \bar{t}; \bar{x}, \bar{y}, z, \bar{t} + 1/2; \bar{x}, \bar{y}, \bar{z}, \bar{t} + 1/2.$$

The above space group can also describe properly our model of mixed modulation. However, it strictly restricts the phase shifts between the occupational

and displacive waves. To analyse this subject we use the following notation for possible modulating waves for the μ th atom:

$$p^\mu(\bar{x}_4^\mu) = p_0^\mu + p_c^\mu \cos(2\pi\bar{x}_4^\mu) + p_s^\mu \sin(2\pi\bar{x}_4^\mu)$$

$$u_i^\mu(\bar{x}_4^\mu) = u_i^{\mu,c} \cos(2\pi\bar{x}_4^\mu) + u_i^{\mu,s} \sin(2\pi\bar{x}_4^\mu),$$

$$i = x, y, z.$$

Compared to work by Kucharczyk *et al.*, the order parameter S has been replaced by the probability function $p^\mu = p_0^\mu = 0.5$ in the paraelectric phase and $0 < p^\mu < 1$ for the IC structure of the AF phase. Although it was shown that u_y^μ plays the dominant role as a displacement amplitude, the two other components will also be considered.

In the $P_{1\ s\ 1}^{I\ m\ m\ m}$ group all atoms occupy special positions. Thus, in addition to the restrictions on positional and thermal parameters there are restrictions on modulation parameters as listed in Table 1. It is easy to see that the phase shift between p^μ and u_y^μ should be equal to 0 or 180°, which is in accordance with the study by Heine *et al.* (1985) and contrary to the arbitrarily chosen value of $\pm 90^\circ$ in the work by Kucharczyk *et al.* Moreover, the u_z^μ component is also purely sinusoidal, whereas u_x^μ is 90° out of phase with respect to the others. To remove these restrictions and allow the relative phases to be refined the $P_{s\ s\ 1}^{I\ 2\ m\ m}$ group was selected. The elements of this group are as follows:

$$(0, 0, 0, 0); (1/2, 1/2, 1/2, 0) +$$

$$x, y, z, t; x, \bar{y}, \bar{z}, t + 1/2; x, \bar{y}, z, t + 1/2; x, y, \bar{z}, t.$$

This space group leaves the extinction rules unchanged and opens a general position for oxygens (see Table 1).

The refinement was carried out for two models (purely occupational and mixed) in the two space groups discussed above, separately. The least-squares-refinement program based on structure-factor formula (3.4) given by Paciorek & Kucharczyk (1985) has been used. The intensity data, lattice parameters and \mathbf{q} vector [$a = 3.660(4)$, $b = 5.650(8)$, $c = 5.365(1)$ Å, $\mathbf{q} = 0.108(5)\mathbf{a}^*$] were exactly the same as those obtained by Kucharczyk *et al.* (1978) except that the satellite intensities at $h \pm q$, k , l were not averaged and several very weak reflections formerly omitted were taken into account. This gave altogether 98 main and 116 satellite independent reflections. Seven strong reflections were, later, omitted owing to extinction.

We started with the atomic parameters and anisotropic temperature factors published in the paper cited above and during the first cycles only the individual occupational waves (p_c^μ and/or p_s^μ parameters) were refined. Next, all the possible displacive waves were included. During the refinement we were very careful not to exceed a reasonable

Table 2. Modulation parameters and discrepancy indices for the trials with different models

Space group	Modulation parameters		Constraints applied	np*	R indices†		
	refined				R _m	R _s	R
$P1\bar{1}m1$	$p_c^{\text{Na}}, p_c^{\text{N}}, p_c^{\text{O}}$		$p_c^{\text{N}} = p_c^{\text{O}}$	19	0.061	0.162	0.089
$P1\bar{2}m1$	$p_c^{\text{Na}}, p_c^{\text{N}}, p_c^{\text{O}}, p_s^{\text{O}}$		$p_c^{\text{N}} = p_c^{\text{O}}, p_s^{\text{N}} = p_s^{\text{O}}$	20	0.062	0.138	0.083
$P1\bar{1}m1$	$p_c^{\text{Na}}, p_c^{\text{N}}, p_c^{\text{O}}, p_s^{\text{O}}, u_y^{\text{Na,c}}, u_y^{\text{Na,s}}, u_y^{\text{N,c}}, u_y^{\text{N,s}}, u_y^{\text{O,c}}, u_y^{\text{O,s}}$		$p_c^{\text{N}} = p_c^{\text{O}}, u_y^{\text{N,c}} = u_y^{\text{O,c}}$	20	0.055	0.091	0.065
$P1\bar{2}m1\ddagger$	$p_c^{\text{Na}}, u_y^{\text{Na,c}}, u_y^{\text{Na,s}}, p_c^{\text{N}}, p_s^{\text{N}}, p_c^{\text{O}}, u_y^{\text{O,c}}, u_y^{\text{O,s}}$		$p_c^{\text{N}} = p_c^{\text{O}}, p_s^{\text{N}} = p_s^{\text{O}}$	24	0.055	0.082	0.063
$P1\bar{2}m1$	As above		$u_y^{\text{N,c}} = u_y^{\text{O,c}}, u_y^{\text{N,s}} = u_y^{\text{O,s}}$	28	0.055	0.081	0.063
$P1\bar{2}m1$	As above, plus $u_x^{\text{N,c}}, u_x^{\text{N,s}}, u_x^{\text{O,c}}, u_x^{\text{O,s}}$		No constraints	32	0.055	0.081	0.063
$P1\bar{2}m1$	As above, plus $u_{x,c}^{\text{Na,c}}, u_{x,c}^{\text{Na,s}}$		No constraints	34	0.055	0.087	0.064
$P1\bar{2}m1$	As above, plus $u_{z,c}^{\text{O,c}}, u_{z,c}^{\text{O,s}}$		No constraints	36	0.056	0.093	0.066

* Number of parameters including scale, modulational, positional and anisotropic thermal parameters.

† $R = \sum \|F_o\| - |F_c| / \sum \|F_o\|$ for all reflections collected. R_m for main reflections, only. R_s for satellite reflections, only.

‡ Refinement taken as final solution.

Table 3. Final parameters for the IC structure of NaNO₂

(a) Atomic coordinates and equivalent isotropic temperature factors with e.s.d.'s in parentheses

$$B_{\text{eq}} = 4/3(\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + \beta_{23}bc)$$

Atom	x	y	z	B _{eq} (Å ²)
Na	0	0.53771 (6)	0	3.260 (2)
N	0	0.07787 (9)	0	3.454 (3)
O	0	-0.04058 (9)	0.19297 (5)	4.781 (2)

(b) Anisotropic temperature factors

Atom	β ₁₁	β ₂₂	β ₃₃	β ₂₃
Na	0.0721 (3)	0.0239 (1)	0.0248 (1)	0
N	0.1039 (5)	0.0223 (1)	0.0169 (1)	0
O	0.1147 (3)	0.0325 (2)	0.0295 (1)	0.0053 (1)

(c) Modulational parameters

Atom	p _c	p _s	u _y ^c	u _y ^s
Na	0.219 (3)	0	0.0134 (3)	-0.0022 (8)
N, O	0.231 (3)	-0.102 (5)	0.0069 (1)	-0.0028 (4)

number of free parameters owing to the limited number of reflections available.*

Results and discussion

The final discrepancy indices obtained for the two selected space groups and successive trials using various models of pure occupational and mixed modulations are presented in Table 2. In addition to the specified modulating parameters used, the total number of free parameters is given. All the R factors shown were calculated with unit weights. It is easy to see that purely occupational modulation with space group $P1\bar{1}m1$ leads to an unsatisfactory R_s factor of 0.162. This is, however, a reasonable starting point for checking both the phase shift between the individual waves for the Na⁺ ion and the NO₂⁻ molecule and the actual presence of extra displacive

* Lists of observed and calculated structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP42173 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

components formerly proposed by Kucharczyk *et al.* In the second space group the phase shift of about 22° between the occupational waves of N⁺ and NO₂⁻ has been found, which reduces R_s to 0.138. No further improvement could be reached by applying individual waves to nitrogen and oxygen atoms, thus the molecule was kept rigid by constraining modulational parameters of these atoms.

Starting once more with the centrosymmetric space group ($R_s = 0.162$), but adding the transverse wave with a displacement along y for the NO₂⁻ molecule only, one found that the refinement converged quickly from $R = 0.089$ to $R = 0.065$ mainly due to a drastic lowering in the R_s index, which dropped to 0.091. Adding a similar displacive wave for the Na⁺ ion and turning to the noncentrosymmetric space group so that the relative phases between the waves were free, one obtained the overall R factor of 0.063 and $R_s = 0.082$.

At that stage of refinement, four more parameters were added by removing the constraints on the NO₂ molecule, but no significant improvement was reached.

Further trials were undertaken to check the presence of longitudinal and second transverse (along the z direction) components of the displacive waves, which is not forbidden by symmetry (see Table 1). The longitudinal components u_x^{μ} were proved to be negligibly small compared with u_y^{μ} and lead to no improvement in the refinement. An addition of the u_z^{μ} components also ended with insignificantly small values. Furthermore, the convergence was no longer possible with all parameters free, as indicated by the bottom lines of Table 2. In view of such results we decided to take the refinement of the model marked with ‡ in Table 2 as the final solution. The list of atomic parameters and temperature factors is presented in Table 3.

The main feature of the IC structure in AF, shown in Fig. 1, is thus the presence of weak displacive waves with amplitudes less than 0.08 Å superposed on the main modulating waves of the occupational

type. The displacements of atoms take place along the b axis only. The amplitude of the displacive wave of the Na^+ ion was found to be almost twice as large (0.077 \AA) as that of the NO_2^- molecule (0.042 \AA), with the occupational amplitudes being approximately the same. There are practically no phase shifts between the displacive and occupational waves, which is in accordance with the arguments given by Heine *et al.* (1985) and contrary to previous work by Kucharczyk *et al.* (1978).

The occupational wave was shifted with respect to the displacive one by $9.0 (3.5)^\circ$ and $2.1 (1.1)^\circ$ for Na and NO_2 , respectively. The phase of the Na occupational wave was set to zero ($p_s = 0$) to fix the phase origin. There are, however, larger phase shifts between the individual waves of the Na^+ ion and the NO_2^- molecule. The phase difference between displacive waves is $12.5 (5.5)^\circ$, whereas for occupational waves it is $24.0 (1.1)^\circ$ as shown in Fig. 1. However, one must notice the relatively high uncertainty in the determination of the phases of modulating waves. Such a problem has been mentioned by Yamamoto (1982) in his consideration of modulated structure with predominantly occupational character. It can be

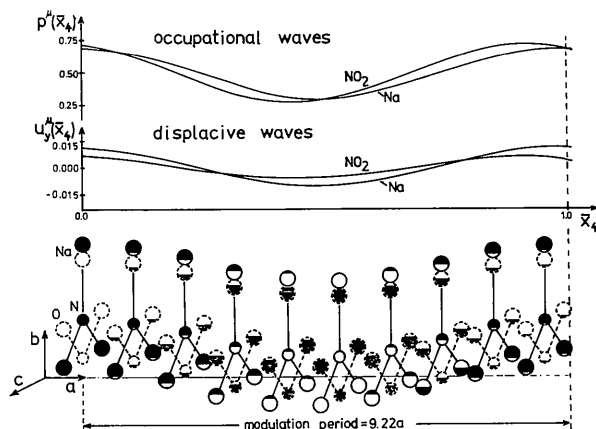


Fig. 1. The modulation waves for the Na^+ ion and the NO_2^- molecule over one period, together with a sketch of the IC structure. Centring molecules in each of the cells are omitted. Displacements of atoms are greatly exaggerated. Atoms drawn with dashed lines represents the equivalent positions given by $(\frac{m}{s}y)$ mirror transformation. The shadowed parts represent the occupational probability.

Table 4. Comparison of minimum and maximum values of bond lengths (\AA) affected by the displacive modulation and angles ($^\circ$) for the structure refined in $P_{1s1}^{1m m m}$ (a) and $P_{ss1}^{12 m m}$ (b)

	(a)		(b)	
	Min.	Max.	Min.	Max.
Na-N	2.549 (2)	2.640 (2)	2.562 (5)	2.635 (5)
Na-O	2.559 (1)	2.635 (2)	2.563 (2)	2.632 (2)
O-N-O	114.19 (5)		114.23 (9)	

seen from Table 2 that the extra displacive waves improve R factors for both main and satellite scattering, whereas an introduction of free phases of the waves positively affects only the subset of satellite reflections. To clear up this point and to find out the significance of these phases, the disturbance of bond lengths over a period of modulation has been examined. The result was that bond lengths are less disturbed when the phase shifts are allowed. The comparison is given in Table 4. For example, the averaged Na-N bond distance of $2.598 (4) \text{ \AA}$ deviates owing to modulation by ± 0.045 and $\pm 0.037 \text{ \AA}$ for fixed and free phases, respectively. This justifies additionally the $P_{2s1}^{12 m m}$ superspace group as the proper one for the IC structure of NaNO_2 .

Helpful comments from Professor K. Łukaszewicz are gratefully acknowledged.

References

- BÖHM, H. (1977). *Eine Erweiterte Theorie der Satellitenreflexe und die Bestimmung der modulierten Struktur des Natriumnitrits*. Habilitationsschrift, Univ. Münster.
- EHRHARDT, K. D. & MICHEL, K. H. (1981). *Z. Phys.* B41, 329-339.
- HEINE, V., LYNDEN-BELL, R. M., MCCONNELL, J. D. C. & McDONALD, J. R. (1985). *Acta Cryst.* Submitted.
- HEINE, V. & MCCONNELL, J. D. C. (1984). *J. Phys. C*, 17, 1199-1210.
- JANNER, A. & JANSSEN, T. (1980). *Acta Cryst.* A36, 399-408.
- KUCHARCZYK, D., PIETRASZKO, A. & ŁUKASZEWICZ, K. (1978). *Ferroelectrics*, 21, 445-447.
- MCCONNELL, J. D. C. & HEINE, V. (1984). *Acta Cryst.* A40, 473-482.
- MICHEL, K. H. (1981). *Phys. Rev. B*, 24, 3998-4007.
- PACIOREK, W. A. & KUCHARCZYK, D. (1985). *Acta Cryst.* A41, 462-466.
- WOLFF, P. M. DE, JANSSEN, T. & JANNER, A. (1981). *Acta Cryst.* A37, 625-636.
- YAMAMOTO, A. (1982). *Acta Cryst.* A38, 87-92.