PHYSICAL REVIEW B VOLUME 31, NUMBER 9 1 MAY 1985

Displacive modulation in the sinusoidal antiferroelectric phase of $NaNO_2$

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(Received 27 July 1984; revised manuscript received 7 February 1985)

The structure of the incommensurate phase of $NaNo_2$ at 162.5 °C is elucidated using x-ray data collected by Böhm [Z. Kristallogr. **148**, 207 (1978)]. The analysis is based on the four-dimensional super-space-group $P^{Immm}_{\bar{1}s1}$, and shows that the sinusoidal modulation of the dipole moment of NO_2 is accompanied by displacive modulation. The displacement wave is a transverse acoustic mode with the wave vector $\mathbf{k}\sim 0.1\mathbf{a}^*$, the amplitude of which is parallel to the *b* axis. This is in phase with the modulation wave of the dipole moment in accordance with theoretical expectation.

I. INTRODUCTION

$NaNO_2$ is known to be transformed from a paraelectric (P) phase (with space group *Immm*) to a ferroelectric (F) phase (with Im2*m*) at about 163 °C with decreasing temperature, passing through a sinusoidal antiferroelectric (SA) phase. The P phase is a disordered phase in which Na and NO_2 occupy two equilibrium positions with the same occupation probability of 0.5. On the other hand, these positions are occupied with different probabilities in the F phase (Fig. 1). The SA phase appears in a narrow temperature range of about 1.5 °C between the F and P phases. This phase has been described as a sinusoidal modulation of the electric dipole moments (polarization) parallel to the *b* axis, which is caused by the periodic change of the occupancies of Na ions and NO_2 molecules in the two equilibrium positions (occupational modulation).[1-4] The fundamental wave vector of the modulation wave changes continuously from about $\mathbf{a}^*/8$ to $\mathbf{a}^*/10$ with decreasing temperature, indicating that the SA phase is the incommensurate phase. The appearance of the SA phase has been explained theoretically using the Ising model with ferroelectric coupling for the nearest layers normal to the *a* axis and antiferroelectric coupling for the second-nearest layers.[1]

Additional insight about the SA phase has been gained from a detailed x-ray study: Kucharczyk *et al.*[5] have shown that the occupational modulation in $NaNO_2$ is accompanied by the condensation of the transverse acoustic mode (displacive modulation). This is understood theoretically as a bilinear coupling term between the polarization and the shear strain in the free energy.[6] A microscopic theory shows that the coupling originates from the interaction between the rotational mode of NO_2 molecules around the *c* axis and the transverse acoustic mode.[7] The theory elucidates the essential role of the coupling for the occurrence of the SA phase: The condensation of the acoustic mode stabilizes the SA phase with respect to the large thermal fluctuations[3,8] which are expected to destroy the weak stabilization effect originating from the dipole-dipole interaction.[9]

From theoretical considerations, the super-space-group of the SA phase is considered to be $P^{Immm}_{\bar{1}s1}$.[10-13] This super-space-group is consistent with the facts that the phase transition from the SA phase to the P phase is of second order[2] and no spontaneous polarization has been observed in the SA phase. The super-space-group restricts the relative phase between the polarization wave and the displacement wave: The phase difference must be 0 or π. Either 0 or π is realized as the coupling term between the rotational mode and the acoustic mode in the free energy is positive or negative.[7,10] Therefore the determination of the sign is important for better understanding of the microscopic origin of the phase transition of $NaNO_2$. This is expected to be positive from theoretical investigations.[10] There are, however, several terms with positive and negative signs and the theoretical determination of the total sign seems to be difficult.

The phase difference can be determined in principle using x-ray analysis. One attempt has been made to determine both the polarization and displacive modulations.[5] The analysis is based on a model in which the phase of the polarization wave is different by $\pi/2$ from that of the displacement wave. This leads to the super-space-group P^{I2mm}_{ss1} which allows spontaneous polarization along the *a* axis. Since no experimental evidence of spontaneous polarization has been reported, the point group of the average structure is considered to be *mmm*. In the theory of super-space-groups, the point group is isomorphic to the

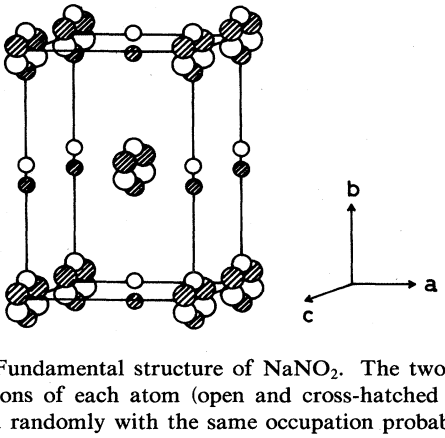

FIG. 1. Fundamental structure of $NaNO_2$. The two equilibrium positions of each atom (open and cross-hatched circles) are occupied randomly with the same occupation probability in the paraelectric phase. Small, middle, and large circles represent Na, N, and O atoms, respectively.

point group of the average structure.[14] If the SA phase has this super-space-group, this phase has a pathological nature because the point symmetry of the super-space-group, which is isomorphic to *mm*2, is lower than that of the average structure, *mmm*. In order to clarify the discrepancy between the super-space-groups deduced from theory and experiment, we carry out the structure analysis of the SA phase based on the super-space-group $P_{\bar{1}s1}^{Immm}$ in this paper and compare the result with that of the model based on P_{ss1}^{I2mm}.

The present analysis is made by using the x-ray data collected at 162.5 °C by Böhm,[3] which include 30 first-order satellite reflections. Although the transition temperature slightly depends on crystal and thermal history[4] and the transition temperature of the crystal used for the data collection is not clear, 162.5 °C is considered to be just above the transition temperature from the F phase to the SA phase.

The present study suggests that the super-space-group is $P_{\bar{1}s1}^{Immm}$. The magnitudes and phases of the two modulation waves are determined based on this symmetry. The results show that the phase difference between the two modes mentioned above is 0 in accordance with theoretical expectations.[10]

II. STRUCTURE DETERMINATION

In the P phase, the crystal has one independent Na atom and one NO_2 molecule in the unit cell. The other Na and NO_2 in the unit cell are related to the independent ones by the centering translation $(E \mid \frac{1}{2},\frac{1}{2},\frac{1}{2})$ included in *Immm*. Each Na or NO_2 occupies two equivalent positions, related, to each other by a mirror plane normal to the *b* axis, $(\sigma_y \mid 0,0,0)$, with the same occupation probability. Two O atoms in a molecule are related to each other by $(\sigma_z \mid 0,0,0)$ (Fig. 1). The F phase has a similar structure but the two sites are occupied with different occupation probabilities, which lead to the lower symmetry *Im*2*m*. The structure allows NO_2 molecules to change their orientation by 180° rotation around the *c* axis.[7]

In the SA phase, satellite reflections appear in the diffraction pattern along the a^* axis in addition to the main reflections existing in the P phase. In this phase, any diffraction vector **h** is expressed as

$$\mathbf{h}=h_1\mathbf{a}^*+h_2\mathbf{b}^*+h_3\mathbf{c}^*+h_4\mathbf{k}$$

with four integers h_1-h_4 and $\mathbf{k}=k_1\mathbf{a}^*$, where $\mathbf{a}^*$, $\mathbf{b}^*$, $\mathbf{c}^*$ are the reciprocal unit vectors for the fundamental structure and **k** is the fundamental wave vector of the modulation waves. The reflections with indices $h_1h_2h_3 0$ indicate the main reflections while those with $h_1h_2h_3 \pm n$ represent the *n*th-order satellite reflections. The symmetry of this phase is described by a four-dimensional space group (super-space-group).[13] From group-theoretical considerations, the super-space-group of this phase is considered to be $P_{\bar{1}s1}^{Immm}$ or P_{ss1}^{I2mm} (Refs. 11 and 12). The centering translation $(E \mid \frac{1}{2},\frac{1}{2},\frac{1}{2},0)$ in these super-space-groups leads to the reflection condition $h_1+h_2+h_3=2n$ which is observed for general reflections $h_1h_2h_3h_4$. (We use the notation employed in a previous paper:[15] In the symmetry operator of the super-space-group, the translation vector is expressed by unit-vector components in four-dimensional space, while the rotation operator is represented by the Seitz notation in three-dimensional space.) Another reflection condition derived from the hyper-glide-plane $(\sigma_y \mid 0,0,0,\frac{1}{2})$, $h_4=2n$ for $h_1 0 h_3 h_4$, is found from the extinction of the first-order satellite reflections, although the second-order satellites are very weak in intensity, if any, and are not observed.[3,13]

The super-space-groups are consistent with the fact that the SA phase is transformed into the P phase via a second-order phase transition with increasing temperature. As is well known, the second-order phase transition restricts the possible symmetry of the SA phase: The difference in the electron density $\delta\rho=\rho^{\mathrm{SA}}-\rho^{\mathrm{P}}$ is expressed in terms of the basis of an irreducible representation of the P phase,[16] where ρ^{SA} and ρ^{P} are the electron-density functions of the SA and P phases. Therefore, $\delta\rho$ must be a basis function of the irreducible representations at $\mathbf{k}=k_1\mathbf{a}^*$. Of the four representations at this point, the fourth representation[17] leads to the super-space-group $P_{\bar{1}s1}^{Immm}$ or P_{ss1}^{I2mm} (Ref. 18). For the reason mentioned previously, the former is considered to be the true symmetry of the SA phase. Therefore, we first analyze the structure based on this symmetry and later we compare the results with those of another model with the latter symmetry in the following section.

In the incommensurate structure, the occupation probability and the displacement of an atom located at **x** in the fundamental structure are periodic functions of $\mathbf{k}\cdot\mathbf{x}$. These can be expressed as a Fourier series.[15] The occupational modulation waves of the two sites [related with $(\sigma_y \mid 0,0,0)$ in the P phase] are related via the hyper-glide-plane $(\sigma_y \mid 0,0,0,\frac{1}{2})$. This requires that the average occupancies of the two sites be the same but allows sinusoidal occupational modulations, keeping the total occupation probability of the two-site unity[19] [see Eqs. (1) and (2) below]. The super-space-group also allows sinusoidal displacive modulations of the two sites, of which one is related to the other by the same hyper-glide-plane. Similarly, the modulation waves of two oxygen atoms in a NO_2 molecule are related by the hyper-mirror-plane $(\sigma_z \mid 0,0,0,0)$. The modulation waves for the other Na and NO_2 in the unit cell are obtained from those of the independent ones by the centering translation $(E \mid \frac{1}{2},\frac{1}{2},\frac{1}{2},0)$. As a consequence, only one site for each atom is independent in the SA phase, the same as in the P phase.

In the present case, all the observed satellite reflections are of first order,[3] so that we need consider only the zeroth- and first-order terms in the Fourier series and can neglect higher-order terms.[19] In addition, we consider only the transverse acoustic mode with displacement parallel to the *b* axis for the displacive modulation, which is considered to be important in the present case.[5,7] In such a simple model, the occupation probabilities of the two sites P^1 and P^2 located at $\mathbf{x}^1$ and $\mathbf{x}^2$ in the fundamental structure (Fig. 1) are written as

$$P^1=\tfrac{1}{2}+P_1\sin[2\pi(\mathbf{k}\cdot\mathbf{x}^1)]\ , \tag{1}$$

$$P^2=\tfrac{1}{2}-P_1\sin[2\pi(\mathbf{k}\cdot\mathbf{x}^2)]\ , \tag{2}$$

TABLE I. Positional and thermal parameters of the average structure at 162.5 °C taken from Böhm (Ref. 3). The equivalent isotropic temperature factor B_{eq} is estimated from the anisotropic temperature factor B_{ij} by $\frac{4}{3}(B_{11}a^2+B_{22}b^2+B_{33}c^2)$. The temperature factors B_{23} of Na and N vanish owing to their site symmetries.

	Na	N	O
x	0.0	0.0	0.0
y	0.541	0.078	−0.034
z	0.0	0.0	0.196
B_{11}	0.079	0.115	0.123
B_{22}	0.033	0.031	0.058
B_{33}	0.042	0.010	0.031
B_{23}	0.0	0.0	0.011
B_{eq}	4.44	3.77	5.88

with the common Fourier amplitude P_1 because of the presence of the hyper-glide-plane $(\sigma_y \mid 0,0,0,\frac{1}{2})$. Similarly the displacements of the two sites, v^1 and v^2, from $\mathbf{x}^1$ and $\mathbf{x}^2$ are written as

$$v^1=v_1\sin[2\pi(\mathbf{k}\cdot\mathbf{x}^1)]\ , \tag{3}$$

$$v^2=v_1\sin[2\pi(\mathbf{k}\cdot\mathbf{x}^2)] \tag{4}$$

with the common Fourier amplitude v_1.

The temperature factor can change periodically in the SA phase. We use the anisotropic temperature factor for the spatially homogeneous part (the zeroth-order Fourier amplitude) according to previous work[3] while an isotropic one is assumed for the first-order Fourier amplitude in order to reduce the number of parameters. The temperature factors of the two sites have the following forms:

$$B_{ii}^1=B_{ii0}+\tfrac{1}{4}(a_i^*)^2B_1\sin[2\pi(\mathbf{k}\cdot\mathbf{x}^1)]\quad (i=1,2,3)\ , \tag{5}$$

$$B_{ii}^2=B_{ii0}-\tfrac{1}{4}(a_i^*)^2B_1\sin[2\pi(\mathbf{k}\cdot\mathbf{x}^2)]\quad (i=1,2,3)\ , \tag{6}$$

where B_{ii0} and B_1 are the zeroth- and first-order Fourier amplitudes for each atom and a_1^*, a_2^*, and a_3^* represent a^*, b^*, and c^*, respectively. B_{23} for each atom is assumed to be homogeneous. (Only oxygen has nonzero B_{23}. See Table I.)

Equations (1)—(6) show that the modulation waves for the occupation probabilities and the temperature factors of the two sites are 180° out of phase with each other while the modulation waves for the displacement are in phase. In particular, a different temperature factor is, in general, realized for sites one and two. This notably improves the R factor. (See Sec. III.)

TABLE II. The R factor and Fourier amplitudes for the occupation probability P_1, displacement v_1, and temperature factor B_1. The standard deviations are in parentheses.

R	P_1	v_1	B_1^{Na}	B_1^{N}	B_1^{O}
0.087	0.21(1)	0.0062(7)	−0.1(2)	0.9(3)	−0.7(4)

The magnitudes and signs of the Fourier amplitudes, P_1, v_1, and B_1, can easily be determined by using a method described in previous papers.[15,19–22] Since the data used include only satellite reflections, for the atomic coordinates in the fundamental structure and the homogeneous parts of the anisotropic temperature factors of each atom we use the values of the average structure determined by Böhm[3] (Table I) and we fix these values throughout the analysis. The lattice constants $a=3.665$, $b=5.670$, and $c=5.358$ Å are also taken from Ref. 3. The fundamental wave vector $\mathbf{k}$ is assumed to be $0.1\mathbf{a}^*$ and the atomic scattering factors for neutral atoms are employed.[23] The structure has been refined by a least-squares program which minimizes the weighted R factor with unit weight,

$$R_w=\left[\sum(\,|F_0|-|F_c|\,)^2\Big/\sum|F_0|^2\right]^{1/2}\ ,$$

where F_0 and F_c are the observed and calculated structure factors.[15,19]

The final parameters are shown in Table II together with the R factor for the satellite reflections (which is defined by $R=\sum|\,|F_0|-|F_c|\,|/\sum|F_0|$). The R factor of 0.087 is satisfactory in that the satellite intensity is weak.[24] In the analysis, the atomic positions listed in Table I are taken as site one so that the magnitude of the polarization along the b direction is proportional to P^1-P^2. The signs of the Fourier amplitudes of P_1 and v_1 are both positive. This means that the polarization wave along the b axis is in phase with the displacement wave. The schematic representation of the modulation in the SA phase is illustrated in Fig. 2. The present analysis indicates that both the occupational and displacive modulations are weak: The occupancy of each atom changes between 0.29 and 0.71 and the maximum displacement is 0.035 Å.

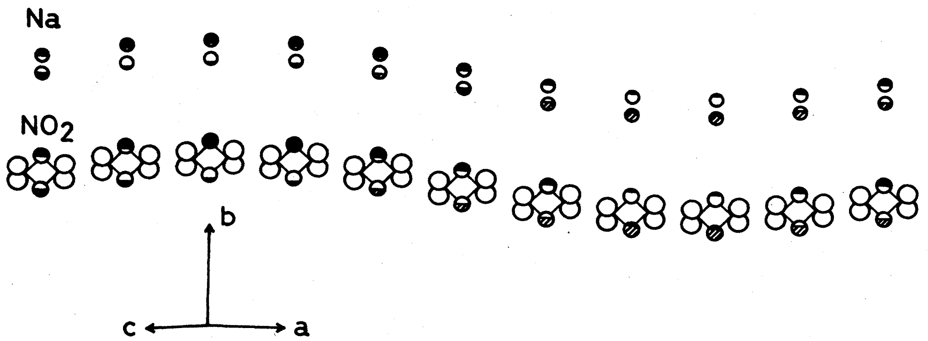

FIG. 2. Schematic picture of the sinusoidal antiferroelectric phase. Shaded and cross-hatched parts represent the occupation probabilities of Na atoms and NO_2 molecules in two equilibrium positions.

III. DISCUSSION

The present analysis shows that the amplitude of the displacement wave at 162.5 °C is 0.0062**b** and that the occupation probability is 0.21. On the other hand, Kucharczyk *et al.*[5] gave 0.011**b** and 0.27 for these quantities under a similar experimental condition. Their model is slightly different from the present one: The modulation waves for the occupation probability and displacement have the phase difference of $\pi/2$ in contrast to the present model and the usual (homogeneous) temperature factor is taken. This model has the super-space-group P_{ss1}^{I2mm} which is a subgroup of $P_{\bar{1}s1}^{Immm}$ and gives the same reflection conditions as the present model as stated in the previous section. The super-space-group P_{ss1}^{I2mm} allows spontaneous polarization along the a axis as is clear from the space group of the average structure $I2mm$ indicated in the upper line of the super-space-group symbol.[13] Although there is neither experimental evidence for nor theoretical implication of the spontaneous polarization in the SA phase, the model based on this symmetry gives a slightly better R factor than the present model as shown in the following.

The super-space-group P_{ss1}^{I2mm} allows displacement of the form $v^1=v_1\sin[2\pi(\mathbf{k}\cdot\mathbf{x}^1)+\phi]$ instead of (3) keeping the relation $v^1=v^2$. Kucharczyk *et al.* consider only a particular case of $\phi=\pi/2$, while the other cases of $\phi=0$ and π reduce to the model described in the previous section which has the higher symmetry $P_{\bar{1}s1}^{Immm}$. In order to compare results, the periodic change in the temperature factor (5) and (6) is taken into account in the present calculation and all the parameters are refined for several values of ϕ. The R factor is plotted against ϕ in Fig. 3. This model shows the best R factor 0.078 at $\phi=0.42\pi$, which is slightly better than the value $R=0.087$ at $\phi=0$. These can be compared with $R=0.13$ obtained from 93 satellites by Kucharczyk *et al.*[5]

We cannot, however, consider that such small R-factor improvement proves the correctness of the model. The model hardly improves the major discrepancy between F_0 and F_c existing in the model described in the previous section as inferred from the R factors. The optimum parameters for a fixed ϕ within $0\leq\phi\leq\pi/2$ give almost the same R factor indicating that ϕ has a large standard deviation: The difference in the R factor is at most 0.009 (Fig. 3). The Hamilton test[25] also cannot reject the present (higher-symmetry) model with confidence greater than 0.5 despite the fact that the lower-symmetry model has a slightly improved R value.

Considering that spontaneous polarization has not been observed and any clear evidence indicating the symmetry P_{ss1}^{I2mm} has not been found from the present analysis, it is reasonable to consider that the real symmetry in the SA phase is $P_{\bar{1}s1}^{Immm}$. The experimental data have been well explained by the model based on this symmetry. In particular the sign of v_1 was definitely determined from the present work. The least-squares refinement initiated from a negative small v_1 converged at the correct positive value. Figure 3 also suggests that a positive v_1 ($\phi=0$) gives a lower R factor than a negative v_1 ($\phi=\pi$).

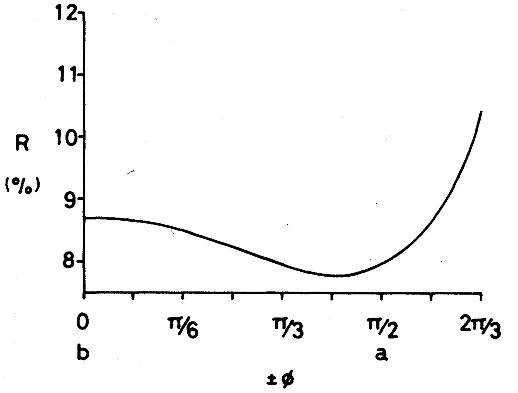

FIG. 3. Change of the R factor with respect to the phase difference ϕ between the modulation waves P^1 and v^1. The points a and b correspond to a model proposed by Kucharczyk *et al.* and the model employed in this paper.

The present work shows that, in addition to displacive modulation, the spatial change in the temperature factor should be taken into account in the analysis. The former improves the R factor by 0.066 compared with the value of Böhm's model in which only the occupational modulation is taken into account. The latter improves furthermore by 0.024 resulting in the R factor of 0.087.

IV. CONCLUSION

x-ray analysis of the SA phase at 162.5 °C elucidates the nature of the condensation of the transverse acoustic mode which is in phase with the polarization wave. The result agrees with recent theoretical results.[10] This supports the theoretical conclusion which states that the bilinear coupling between the rotational mode of NO_2 molecules and the transverse acoustic mode is essential for the occurrence of the SA phase.[7]

ACKNOWLEDGMENT

The author thanks Professor V. Heine for sending a copy of his paper prior to publication.

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