Neutron Diffraction Study of the Low-Temperature Phases of Sodium Oxide Nitrite, Na₃ONO₂

G. Klösters and M. Jansen

Institut für Anorganische Chemie der Universität Bonn, Gerhard-Domagk-Strasse 1, D-53121 Bonn, Germany; and
Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-70569 Stuttgart, Germany

As a function of temperature the nitrite ions in sodium oxide nitrite, Na₃ONO₂, show unique and complex order/disorder phenomena. The crystal structures of the three low-temperature modifications of Na₃ONO₂ have been determined by neutron powder diffraction. In the cubic room-temperature modification (H-Na₃ONO₂, space group $Pm\bar{3}m$) the nitrite ions exhibit a 12-fold orientational disorder. Upon cooling, the orientational disorder of the nitrite ions is reduced by two continuous order processes and one discontinuous phase transition. At $T \approx 240$ K, H-Na₃ONO₂ transforms by a continuous phase transition to tetragonal M-Na₃ONO₂ (space group $I4/mcm$, $a = 6.49174(12)$ Å, $c = 9.19415(59)$ at $T = 195$ K), and the orientational disorder of the nitrite ions is reduced via a continuous order process. The order parameter Q follows the power law $Q \approx (T_C - T)^\beta$ with $T_C = 239.5(6)$ K and $\beta = 0.28(2)$. At $T = 178$ K a discontinuous phase transition ($\Delta H = 620$ J/mol) takes place and M-Na₃ONO₂ transforms to T-Na₃ONO₂ (space group $P4/mbm$, $a = 6.46513(7)$ Å, $c = 4.62382(6)$ at $T = 125$ K). In T-Na₃ONO₂ the nitrite ions exhibit a 2-fold orientational disorder. At $T \approx 68$ K a second continuous phase transition to TT-Na₃ONO₂ (space group $P\bar{4}2_1m$, $a = 6.45345(6)$ Å, $c = 4.61973(6)$ at $T = 5$ K) takes place and the orientational disorder is further reduced. This order process is characterized by a critical temperature of $T_C = 67.4(2)$ K and a critical exponent of $\beta = 0.21(1)$. © 1999 Academic Press

Key Words: continuous phase transition; orientational disorder; order parameter.

INTRODUCTION

Sodium oxide nitrite Na₃ONO₂ was first synthesized by Zintl and Morawietz in 1937 (1). Assuming that the compound contains the orthonitrite ion "NO_3^{3-}" they called it sodium orthonitrite, Na₃NO₃. In 1977 the structure of sodium orthonitrite was determined by single-crystal X-ray diffraction (2, 3). It has been shown that Na₃NO₃ does not contain an orthonitrite ion, but has to be addressed as an oxide nitrite.

According to the formula $(Na_3O)^+ NO_2^-$, sodium oxide nitrite crystallizes in the anti-perovskite type of structure (space group $Pm\bar{3}m$). The Na_3O^+-substructure constitutes a framework of corner-sharing (ONa_6) octahedra and the nitrite ions occupy the cuboctahedral interstices formed by 12 Na^+ ions of the framework. The incompatibility between the symmetry of the nitrite ion ($2mm$) and its site symmetry ($m\bar{3}m$) is resolved by a 12-fold orientational disorder of the nitrite ion. The disorder of the nitrite ion can be described by 6 nitrogen split sites (occupancy of 1/6), forming an octahedron, and 24 oxygen split sites (occupancy of 1/12), forming a truncated octahedron. The primitive cubic unit cell of H-Na₃ONO₂ (the room-temperature modification of Na₃ONO₂) is shown in Fig. 1, the atomic coordinates are given in Table 1.

By low-temperature Guinier diffractometry in the temperature range RT > T > 140 K two low-temperature modifications of Na₃ONO₂ were identified (4), a second cubic modification (M-Na₃ONO₂), stable between 220 and 160 K, and a tetragonal modification (T-Na₃ONO₂) below 160 K. The similarities of the observed diffraction patterns of the three polymorphs indicate that the main structural feature of H-Na₃ONO₂, the anti-perovskite structure, remains unchanged during the phase transitions. Therefore, it was suggested that the observed phase transitions are caused by order/disorder processes of the nitrite ions. For T-Na₃ONO₂ a structural model in space group $P\bar{4}2_1m$ was proposed assuming an anti-ferroelectric ordering of the nitrite ions accompanied by a tetragonal distortion of the Na_3O^+-framework. The present paper reports the results of a neutron powder diffraction study of Na₃ONO₂ (5, 6) in the temperature range 239 K > T > 5 K.

EXPERIMENTAL

Sodium oxide nitrite Na₃ONO₂ was prepared by solid state reaction of sodium oxide Na₂O and sodium nitrite NaNO₂ as previously described (4). For the subsequent
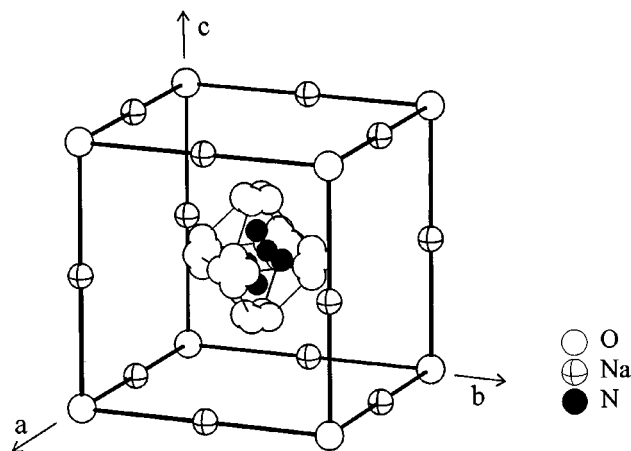
FIG. 1. Unit cell of H-Na$_3$ONO$_2$.

TABLE 1
Atomic Coordinates of H-Na$_3$ONO$_2$ (Space Group $Pm\bar{3}m$, $a = 4.617$ Å)

Atom	Site	x	y	z	SOF
O$_1$	1a	0	0	0	1
Na$_1$	3d	1/2	0	0	1
N$_1$	6f	0.3980	1/2	1/2	1/6
O$_2$	24l	1/2	0.5500	0.7227	1/24

analyses the product was transferred into a thin-walled vanadium container (for neutron diffraction) and a stainless steel crucible (for DSC measurement) under an inert atmosphere (glove box).

Neutron diffraction data at $T = 5$ K (TT-phase), $T = 125$ K (T-phase), and $T = 195$ K (M-phase) were collected on the diffractometer D1A (7, 8) at the Institut Laue-Langevin, Grenoble, with a neutron wavelength of $\lambda = 1.964(2)$ Å. The data were collected over a range $6° < 2\theta < 156°$ with a total collection time of about 12 h and analyzed by the Rietveld method using the program FULLPROF (9). Since the sample contained small amounts of sodium oxide, the profile fits were performed as two-phase refinements with sodium oxide (10) as the second phase.

In order to measure the peak intensities of the lowest order superlattice reflections in TT- and M-Na$_3$ONO$_2$ as a function of temperature, the sample was cooled down slowly, and several data sets were recorded at intermediate temperatures in the two temperature ranges 5–75 K and 195–240 K. At each temperature the system was allowed to equilibrate for 0.5 h, and a data set was collected covering the range $20° < 2\theta < 80°$ with a collection time of 1 h. Peak intensities were obtained by fitting Gaussian profiles to the data, and the intensities of the superlattice reflections were scaled to the intensity of an adjacent regular reflection.

Thermoanalytical measurements were carried out using a Perkin Elmer DSC-2C in the temperature range from 140 K to RT (heating rate 10 K/min).

RESULTS AND DISCUSSION

Polymorphism of Na$_3$ONO$_2$

The low-temperature neutron diffraction investigations on Na$_3$ONO$_2$ reveal the existence of four polymorphs depending on temperature. Na$_3$ONO$_2$ transforms at $T_{H-M} \approx 240$ K from the cubic room temperature modification (H-Na$_3$ONO$_2$) to a second cubic modification (M-Na$_3$ONO$_2$), at $T_{M/T} = 178$ K to a tetragonal modification (T-Na$_3$ONO$_2$), and at $T_{T/TT} \approx 68$ K to TT-Na$_3$ONO$_2$ which is stable down to $T = 5$ K and is tetragonal as well. The neutron diffraction patterns of the four phases are shown schematically in Fig. 2 with the reflections of H-Na$_3$ONO$_2$ indexed.
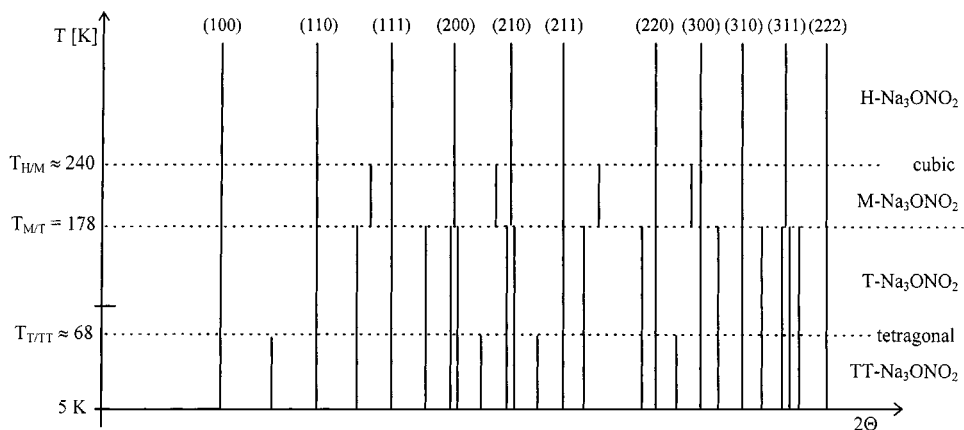

FIG. 2. Schematic representation of the powder patterns of Na$_3$ONO$_2$ in the temperature range RT $> T >$ 5K.
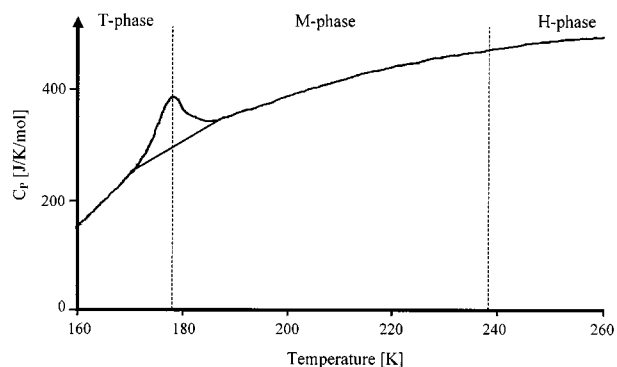
FIG. 3. Molar heat capacity C_p of Na_3ONO_2 in the temperature range 160 K < T < 260 K.

The similarities of the diffraction patterns depicted in Fig. 2 reflect the close structural relationships between the four modifications of Na_3ONO_2. The phase transition from the cubic to the tetragonal modification (M-$Na_3ONO_2 \rightarrow$ T-Na_3ONO_2) is obviously discontinuous. This is confirmed by DSC measurements which reveal a thermal anomaly at $T = 178$ K with an associated enthalpy change of $\Delta H = 620$ J/mol (Fig. 3). By contrast, the two phase transitions between the two cubic and between the two tetragonal modifications (H-$Na_3ONO_2 \rightarrow$ M-Na_3ONO_2 and T-$Na_3ONO_2 \rightarrow$ TT-Na_3ONO_2, respectively) are apparently continuous. These phase transitions are indicated by superlattice reflections which emerge without any resolvable discontinuity on decreasing temperature. The lack of any other significant changes in the diffraction patterns (Fig. 2) suggests that continuous order/disorder processes take place in M-Na_3ONO_2 and TT-Na_3ONO_2. This interpretation is supported by DSC measurements which do not show any evidence for a phase transition at about $T \approx 240$ K (Fig. 3).

The crystal structures of the three low temperature modifications of Na_3ONO_2 were determined by Rietveld analysis of the neutron diffraction data recorded at T = 195 K (M-Na_3ONO_2), $T = 125$ K (T-Na_3ONO_2), and $T = 5$ K (TT-Na_3ONO_2). The refinement conditions and standard R factors are given in Table 2, the observed and calculated diffraction patterns are depicted in Fig. 4.

Crystal Structure of T-Na_3ONO_2

The tetragonal unit cell of T-Na_3ONO_2 can be derived from the cubic cell of H-Na_3ONO_2 by the transformation:

$$\begin{pmatrix} a \\ b \\ c \end{pmatrix}_T \approx \begin{pmatrix} 1 & \bar{1} & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \cdot \begin{pmatrix} a \\ b \\ c \end{pmatrix}_H$$

The observed reflection conditions ($0kl$: $k = 2n$, $0k0$: $k = 2n$) are consistent with the space groups $P4bm$ (No. 100), $P\bar{4}b2$ (117), or $P4/mbm$ (127). Structure refinement of T-Na_3ONO_2 converges quickly in space group $P4/mbm$ (127). The final positional parameters are given in Table 3. The unit cell of T-Na_3ONO_2 is shown in Fig. 5.

In T-Na_3ONO_2 the nitrite ions are twofold orientationally disordered, which can be readily refined based on a split atom model. The geometry of the nitrite ion ($r_{N,O} = 1.249$ Å; < ONO = 117.5°) does not deviate principally from its geometry in $NaNO_2$ ($r_{N-O} = 1.240$ Å; < ONO = 114.9°) (11), so that the nitrite ions in Na_3ONO_2 can be considered as rigid bodies keeping the same geometry when the temperature is lowered. The deviation of the c/a-ratio ($c/a = 0.715$) from a strictly cubic metric ($c/a = 1/\sqrt{2} = 0.707$) is quite small, indicating that the Na_3O^+-framework is but slightly distorted. Inspection of the atomic parameters in Table 3 shows that the distortion of the framework can be attributed to a displacement of the sodium ions at site Na2, which are shifted from their "regular" positions at (1/4, 1/4, 1/2) toward the oxygen atoms of the adjacent nitrite ions. Apparently, the distortion of the framework is caused by attractive interactions between sodium ions of the framework and oxygen atoms of the nitrite ions. This displacement of the Na^+ ions at site Na2 decreases the O–O distances of the Na_3O matrix in the a/b plane in comparison to the O–O distances along the c axis, so that the cubic framework, and thereby the crystal structure, transforms to a tetragonal metric.

Crystal Structure of TT-Na_3ONO_2

The diffraction pattern of TT-Na_3ONO_2 has been indexed in analogy to the tetragonal unit cell of T-Na_3ONO_2. The additional superlattice reflections in TT-Na_3ONO_2 (see Fig. 1) are violating the reflection condition ($0kl$: $k = n$), while the condition ($0k0$: $k = 2n$) survives. Thus, possible space groups are $P42_12$ (No. 90) and $P\bar{4}2_1m$ (No. 113). Structure refinement converges in space group $P\bar{4}2_1m$ (No. 113). The final positional parameters of TT-Na_3ONO_2 are given in Table 4.

The structure of TT-Na_3ONO_2 is closely related to the one of T-Na_3ONO_2. Both structures exhibit the same twofold orientational disorder of the nitrite ions and differ only in the relative occupancy of these orientations. While in T-Na_3ONO_2 each nitrite ion occupies the two orientations with equal probability, in TT-Na_3ONO_2 the nitrite ion prefers one of these. By their preferred orientation the nitrite ions induce a superstructure with the resultants of the dipoles on each site aligned in an antiferroelectric sense.

TABLE 2
Refinement Conditions for the Three Structure Refinements Presented

	M-Na$_3$ONO$_2$ $T = 195$ K	T-Na$_3$ONO$_2$ $T = 125$ K	TT-Na$_3$ONO$_2$ $T = 5$ K
	Global data		
λ (Å)	1.964 (1)	1.964 (1)	1.964 (1)
2θ range (°)	6–155.85	6–155.85	6–155.85
$\Delta 2\theta$ (°)	0.05	0.05	0.05
Zero shift (°)	0.156 (2)	0.169 (2)	0.147 (2)
Profile function	Pseudo-Voigt	Pseudo-Voigt	Pseudo-Voigt
Profile parameters	$U = 0.134$ (4)	$U = 0.113$ (2)	$U = 0.109$ (2)
	$V = -0.377$ (11)	$V = -0.319$ (6)	$V = -0.299$ (6)
	$W = 0.357$ (6)	$W = 0.331$ (5)	$W = 0.322$ (4)
	$\eta = 0.114$ (19)	$\eta = 0.159$ (15)	$\eta = 0.159$ (13)
Asymmetry parameter	0.0588 (63)	0.0857 (60)	0.0875 (53)
Number of refined parameters	27	25	27
	Na$_3$ONO$_2$ related data		
Space group	$I4/mcm$	$P4/mbm$	$P\bar{4}2_1m$
Weight fraction (%)	99.79	99.41	99.78
Reflection number	67	69	79
Distance constraints	4	—	—
Cell parameters (Å)	$a = 6.49174$ (12)	$a = 6.46513$ (7)	$a = 6.45345$ (6)
	$c = 9.19415$ (59)	$c = 4.62382$ (6)	$c = 4.61973$ (6)
R_{Bragg} (%)	5.02	4.26	3.93
	Na$_2$O related data		
Space group	$Fm\bar{3}m$	$Fm\bar{3}m$	$Fm\bar{3}m$
Weight fraction (%)	0.21	0.59	0.22
Reflection number	11	11	11
Cell parameter (Å)	$a = 5.54756$ (48)	$a = 5.54123$ (36)	$a = 5.53622$ (29)
Global B_{iso} (Å^2)	-0.722 (608)	-0.187 (412)	-1.659 (421)
R_{Bragg} (%)	11.8	9.50	11.6
	Conventional Rietveld factors		
R_P (%)	19.9	12.7	11.9
R_{WP} (%)	18.3	14.5	13.1
R_{Ex} (%)	12.20	10.98	8.61
χ^2	2.25	1.74	2.31

Since the intensities of the superlattice reflections in TT-Na$_3$ONO$_2$ increase over a wide temperature range, one can conclude that the reduction of the orientational disorder of the nitrite ions is not achieved by a discontinuous phase transition like those that have been observed in many inorganic salts containing polyatomic ions (12), but proceeds via a continuous order/disorder process. The fully disordered state of this order/disorder process is characterized by the disorder of the nitrite ions in T-Na$_3$ONO$_2$ and the (hypothetical) totally ordered state is characterized by an anti-ferroelectric alignment of the nitrite ions (Fig. 6).

The degree of order in TT-Na$_3$ONO$_2$ is defined by the difference in the occupancies of the sites Na2, N1, O2 and Na3, N2, O3 (Table 4), which can conveniently be expressed by the order parameter Q:

$$\text{Occupancy (Na2)} = \text{Occupancy (N1)}$$
$$= \text{Occupancy (O2)} = (1 + Q)/2$$

$$\text{Occupancy (Na3)} = \text{Occupancy (N2)}$$
$$= \text{Occupancy (O3)} = (1 - Q)/2.$$

At a temperature of $T = 5$ K the order parameter equals $Q = 0.80$ (Table 4).

Since the intensities of the superlattice reflections I_{SL} are proportional to Q^2, the order parameter as a function of temperature can be calculated from I_{SL}. Figure 7 shows the measured intensity of the lowest superlattice reflection
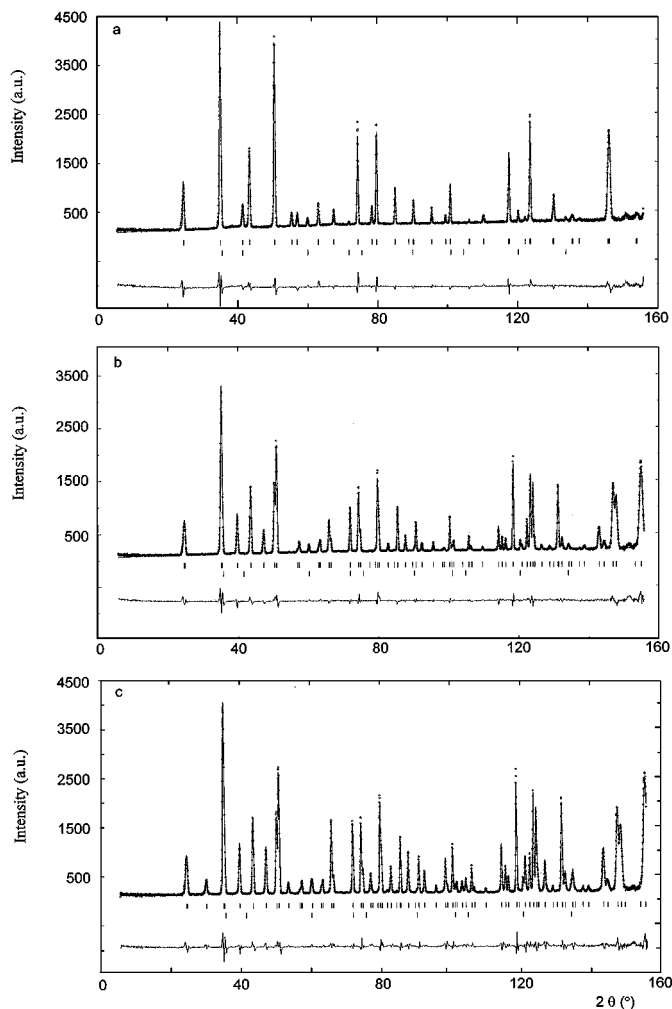
FIG. 4. Observed, calculated, and difference neutron powder diffraction profiles of (a) M-Na_3ONO_2 ($T = 195$ K), (b) T-Na_3ONO_2 ($T = 125$ K), and (c) TT-Na_3ONO_2 ($T = 5$ K). Tic-marks below the diffractogram represents Na_3ONO_2 (top) and Na_2O (bottom).

FIG. 5. Unit cell of T-Na_3ONO_2; origin shifted by $(0, 0, 1/2)$.

I_{011} scaled to the intensity of the adjacent regular reflections $(I_{001} + I_{110})$ and, on a second axis, to the calculated values of Q as a function of temperature. The two axes are linked by the data point at $T = 5$ K where an intensity ratio of $I_{011}/(I_{001} + I_{110}) = 0.32$ has been measured and an order parameter of $Q = 0.80$ has been determined by Rietveld refinement.

If the order parameter Q represents the primary order parameter of the continuous phase transition T-$Na_3ONO_2 \to$ TT-Na_3ONO_2, it should be related to the reduced temperature $(T_C - T)$ by a power law (13):

$$Q \propto (T_C - T)^\beta.$$

The critical exponent β is characteristic for the type of phase transition, and T_c is the critical temperature at which the superlattice reflections appear. A reliable determination of the critical exponent β is not possible due to the small number of data points in the temperature range around T_C. Fitting the data points between $50 K < T < 70 K$ yields a critical temperature of $T_C = 67.4$ K and an exponent of $\beta = 0.21$. As shown in Fig. 7 the order parameter Q does not converge to $Q \to 1$ at $T \to 0 K$. Obviously the system was not in thermodynamic equilibrium at low temperatures, and metastable, disordered states were preserved.

TABLE 3
Positional Parameters and Isotropic Thermal Parameters of T-Na_3ONO_2 ($T = 125$ K)

Atom	Site	x	y	z	B (Å^2)	SOF
O_1	$2b$	0	0	1/2	0.230 (42)	1
Na_1	$2a$	0	0	0	0.473 (66)	1
Na_2	$4h$	0.2320 (3)	0.2680 (3)	1/2	1.097 (56)	1
N_1	$4f$	0	1/2	0.8823 (4)	1.183 (43)	1/2
O_2	$8k$	0.6168 (2)	0.1168 (2)	0.9775 (13)	1.471 (55)	1/2

TABLE 4
Positional Parameters and Isotropic Thermal Parameters of TT-Na_3ONO_2 ($T = 5$ K)

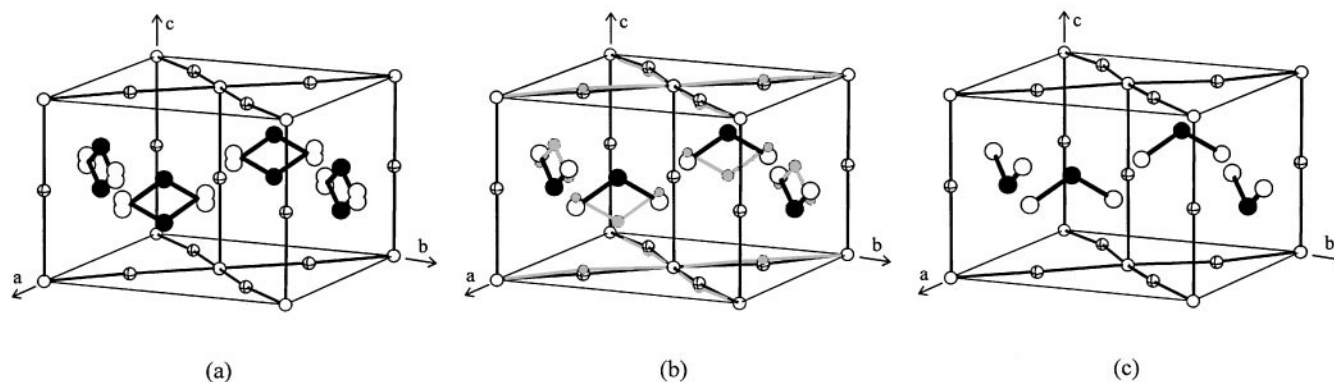| Atom	Site	x	y	z	B (Å^2)	SOF
O_1	$2b$	0	0	1/2	0.141 (39)	1
Na_1	$2a$	0	0	0	0.248 (62)	1
Na_2	$4e$	0.2286 (3)	0.2714 (3)	0.4965 (17)	0.675 (51)	0.901 (2)
Na_3	$4e$	0.2286 (3)	0.2714 (3)	0.5035 (17)	0.675 (51)	0.099 (2)
N_1	$2c$	0	1/2	0.1197 (4)	0.651 (35)	0.901 (2)
N_2	$2c$	0	1/2	0.8803 (4)	0.651 (35)	0.099 (2)
O_2	$4e$	0.6168 (2)	0.1168 (2)	0.0238 (6)	0.666 (40)	0.901 (2)
O_3	$4e$	0.6168 (2)	0.1168 (2)	0.9762 (6)	0.666 (40)	0.099 (2)

FIG. 6. The continuous order process in TT-Na$_3$ONO$_2$. The high-temperature limit of the order process ($Q = 0$); unit cell of T-Na$_3$ONO$_2$ (67.5 K $< T <$ 178 K), origin shifted by (0, 0, 1/2). (b) In the mediate temperature range of the order process ($0 < Q < 0.8$); the atoms on sites Na3, N2, and O3 are depicted as gray spheres; unit cell of TT-Na$_3$ONO$_2$ (67.5 K $> T >$ 5 K), origin shifted by (0, 0, 1/2). (c) The (hypothetical) low temperature limit of the order process ($Q = 1$).

Crystal Structure of M-Na$_3$ONO$_2$

Based on a cubic unit cell with a cell constant which is twice the cell constant of the H-phase all reflections of the M-phase can be indexed. Analysis of the reflection conditions leads to a face centered lattice (extinction symbol: $F{-}{-}{-}$). It is, however, impossible to construct a reasonable structure model based on a face centered cubic unit cell as determined and it had already been suspected (4) that the structure of the M-phase exhibits only cubic metric but not cubic symmetry. Based on a detailed solid state NMR study which will be published elsewhere, we have deduced a structure model of the M-phase with tetragonal symmetry (space group $I4/mcm$). The unit cell is related to the cell of H-Na$_3$ONO$_2$ by the transformation

$$\begin{pmatrix} a \\ b \\ c \end{pmatrix}_M \approx \begin{pmatrix} 1 & \bar{1} & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 2 \end{pmatrix} \cdot \begin{pmatrix} a \\ b \\ c \end{pmatrix}_H .$$
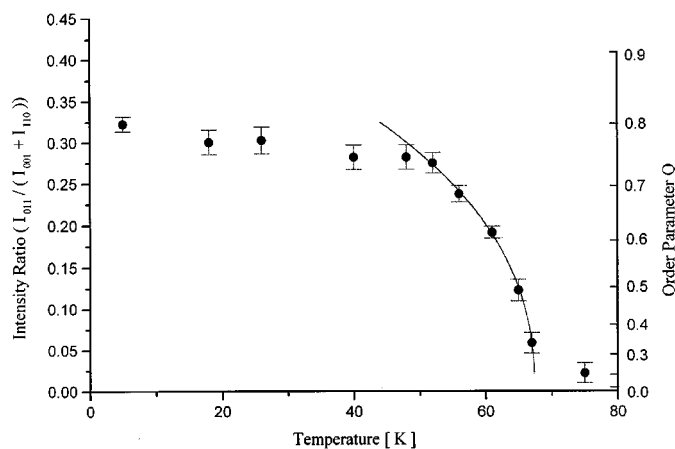

FIG. 7. The order parameter Q as a function of temperature in TT-Na$_3$ONO$_2$.

The Rietveld refinement was handicapped by the fact that a large number of structural parameters had to be refined while only a relatively small number of observed reflections had been recorded. The structural refinement was performed under the assumption that the H- and M-phase have corresponding atomic positions. This means, that the nitrogen and oxygen split sites of the disordered nitrite ion have a time-averaged symmetry $m\bar{3}m$, so that their spatial coordinates could be described by three "free" parameters, one parameter for the nitrogen sites N1–N3 and two parameters for the oxygen sites O2–O7. Since the refinement program did not make it possible to apply linear combinations of parameter codes, the spatial coordinates of the split sites O6 and O7 had to be described by two additional parameters. A nearly octahedral arrangement of the oxygen atoms O2–O7 was maintained by fixing the geometry of the nitrite ion with two constraints: (1) the distance between nitrogen and oxygen of the nitrite ion was fixed to $r_{N,O} = 1.250$ (5) Å, and (2) the distance between the oxygen atoms was kept at $r_{O,O} = 2.135$ (5) Å. Using these constraints, the symmetry break at the phase transition is solely caused by a different occupation of the atomic sites. The final positional parameters and isotropic thermal parameters are given in Table 5.

Analogous to the order process in TT-Na$_3$ONO$_2$, the nitrite ions in M-Na$_3$ONO$_2$ are subject to a continuous order/disorder transformation with preferred orientations for the nitrite ions. In the high temperature limit of the order process (disordered state) the nitrite ions occupy 12 orientations with equal probability and the nitrogen (N1–N3) as well as the oxygen split sites (O2–O7) are occupied equally (Table 5). Over an intermediate temperature range the nitrite ions increasingly occupy 2 of these 12 orientations with decreasing temperature. These two preferred orientations of the nitrite ions are represented by the split sites N1 and O2 (Table 5). Finally, in the low temperature limit (ordered

TABLE 5
Positional Parameters and Isotropic Thermal Parameters of M-Na$_3$ONO$_2$ ($T = 195$ K)

Atom	Site	x	y	z	B (Å)	SOF
O$_1$	4a	0	0	1/4	0.730 (68)	1
Na$_1$	4c	0	0	0	1.528 (246)	1
Na$_2$	8e	1/4	1/4	1/4	1.641 (145)	1
N$_1$	8g	0	1/2	0.0483 (10)	4.900 (263)	0.386 (2)
N$_2$	8h	0.0493 (10)	0.5493 (10)	0	4.900 (263)	0.057 (2)
N$_3$	8h	0.0493 (10)	0.4507 (10)	0	4.900 (263)	0.057 (2)
O$_2$	16l	0.1161 (2)	0.6161 (2)	$-$0.0195 (6)	2.064 (112)	0.357 (2)
O$_3$	16l	0.1161 (2)	0.3839 (2)	$-$0.0195 (6)	2.064 (112)	0.029 (2)
O$_4$	16l	$-$0.0195 (6)	0.4805 (6)	0.1161 (2)	2.064 (112)	0.029 (2)
O$_5$	16l	$-$0.0195 (6)	0.5195 (6)	0.1161 (2)	2.064 (112)	0.029 (2)
O$_6$	16k	0.0960 (12)	0.6364 (8)	0	2.064 (112)	0.029 (2)
O$_7$	16k	0.0960 (12)	0.3636 (8)	0	2.064 (112)	0.029 (2)

state) only these sites are occupied corresponding to a twofold orientational disorder of the nitrite ion.

The degree of order is defined by the occupancies of the split sites and can be described by an order parameter Q:

$$\text{occupancy (N1)} = (1 + 2Q)/6;$$

$$\text{occupancy (O2)} = (1 + 5Q)/12$$

$$\text{occupancy (N2–N3)} = (1 - Q)/6;$$

$$\text{occupancy (O3–O7)} = (1 - Q)/12.$$

Changing the order parameter from $Q = 0$ to $Q > 0$ breaks the average point symmetry of the disordered nitrite ion. At an order parameter $Q = 0$ the average symmetry of the disordered nitrite ion is described by the point group $m\bar{3}m$, at an order parameter $0 < Q \leq 1$ the point group is reduced to $2/m\ 2/m\ 2/m$. This symmetry break is reflected by the appearance of additional superlattice reflections in the diffraction pattern (M-phase-reflections); i.e., the continuous order process at intermediate temperatures takes place in the M-phase of Na$_3$ONO$_2$. The H-phase of Na$_3$ONO$_2$ represents the disordered state of the order process ($Q = 0$). The low temperature limit of the order process is characterized by a twofold orientational disorder of the nitrite ions; the same kind of disorder is observed in T-Na$_3$ONO$_2$. However, M- and T-phase differ in the type of superstructure which is formed by the nitrite ions. In the low temperature limit of the order process the nitrite ions form a body-centered tetragonal superstructure (space group $I4/mcm$); in T-Na$_3$ONO$_2$, the superstructure is primitive tetragonal (space group $P\bar{4}2_1m$). Therefore, the T-phase of Na$_3$ONO$_2$ does not represent the ordered state of the order process. The described order process is illustrated in Figs. 8a–8c.

At $T = 195$ K an order parameter of $Q = 0.65$ was deduced from the results of a Rietveld refinement. The measured intensities of the lowest superlattice reflection I_{211} (scaled to the intensity of the adjacent regular reflection I_{202}) and the respective order parameter at different temperatures are shown in Fig. 9.

Fitting the data points to the power law

$$I_{SL} \propto Q^2 \propto (T_c - T)^{2\beta}$$

yields a critical exponent of $\beta = 0.28$ (2) and a critical temperature of $T_C = 239.5$ (6) K. The ordered state of the
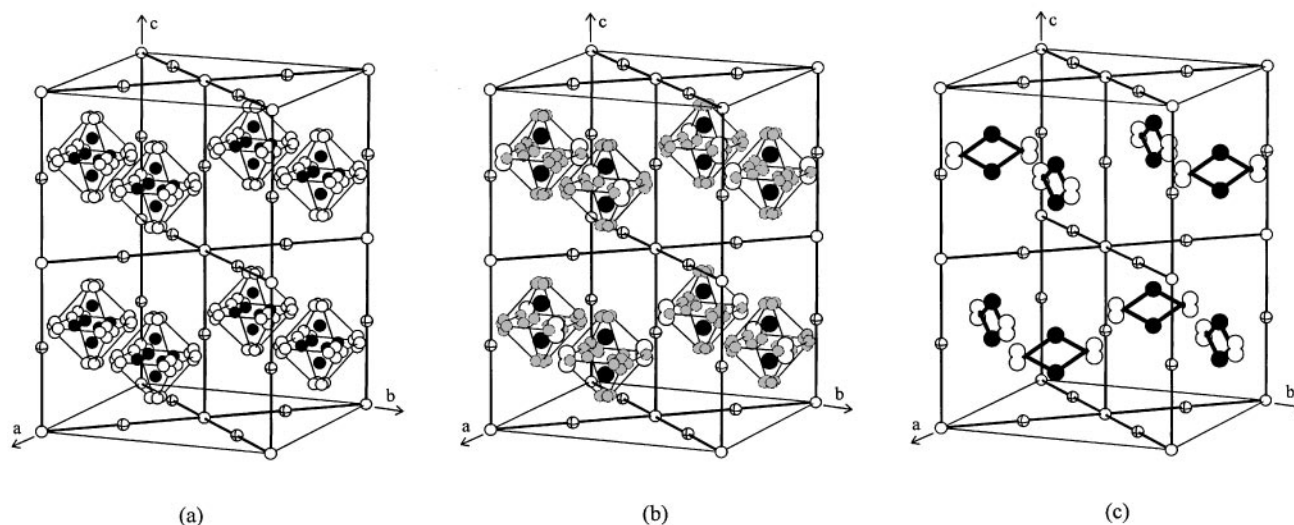

FIG. 8. The continuous order process in M-Na$_3$ONO$_2$. The high temperature limit of the order process ($Q = 0$); crystal structure of H-Na$_3$ONO$_2$ ($T > 239.5$ K). (b) In the mediate temperature range of the order process ($0 < Q < 0.66$; the atoms on sites N2, N3, and O3–O7 are figured as gray atoms; unit cell of M-Na$_3$ONO$_2$ (239.5 K $> T >$ 178 K); origin shifted by (0, 0, 1/4). The (hypothetical) low temperature limit of the order process ($Q = 1$).

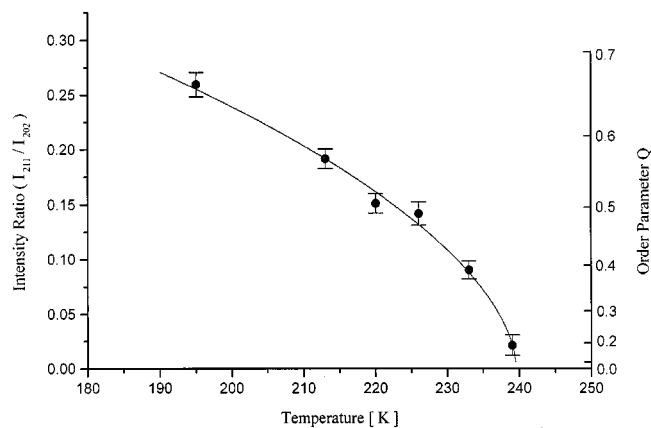**FIG. 9.** The order parameter Q as a function of temperature in M-Na_3ONO_2.

order process is not reached in the temperature range of the M-phase (180–235 K) and the ordered state shown in Fig. 8c is hypothetical.

The cubic metric of the M-phase (tetragonal symmetry) can be understood by comparing the structures of the M- and T-phase. In T-Na_3ONO_2 the tetragonal metric of the structure is a consequence of a distortion of the Na_3O^+-framework with the sodium ions at site Na2 undergoing the largest displacement. These are shifted from their "regular" positions at (1/4, 1/4, 1/2) toward the nearest oxygen atoms of the nitrite ions due to electrostatic interactions. Assuming the same type of electrostatic interactions in M-Na_3ONO_2, these can not distort the framework, since the electrostatic forces acting upon the Na^+ ions compensate each other because of the body centered arrangement of the nitrite ions. This is illustrated in Fig. 10, which shows the coordination of the sodium ions at site Na2 in T-Na_3ONO_2 and in the low temperature limit of M-Na_3ONO_2.

Symmetry Relations

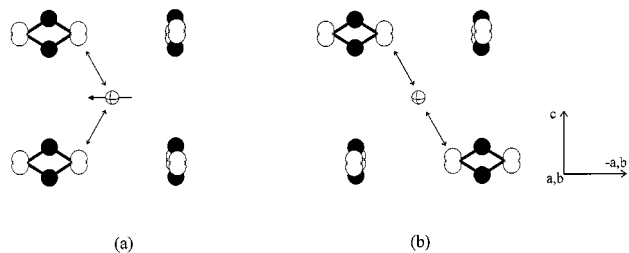The symmetry relations between the space groups of the different phases of Na_3ONO_2 are consistent with the occur-

FIG. 10. The coordination of the sodium ions on site Na2 (a) in T-Na_3ONO_2 and (b) in the low-temperature limit of M-Na_3ONO_2.

rence of two continuous and one discontinuous phase transition. A group–subgroup relationship, which is a prerequisite for continuous phase transitions, exists between the space groups of the H- and the M-phases as well as between those of the T- and the TT-phases. Due to the reduction of the unit cell during the transition between M- and T-phases no group/subgroup relationship can be found for the space groups of the two latter phases. The symmetry breakings, which are accompanied by the two order processes in Na_3ONO_2 can be analyzed in terms of Landau theory. According to Landau theory (13, 14) the structural changes at a continuous phase transition transform like an irreducible representation (active representation) of the high-symmetry space group, which has to fulfill several criteria concerning the symmetry (Landau/Lifshitz conditions). According to the tables of Stokes and Hatch (14), which contain the isotropic subgroups of the 230 space groups and the irreducible representations connecting them, the active representation of the phase transition H-$Na_3ONO_2 \leftrightarrow$M-$Na_3ONO_2$ is R_3^- and the phase transition is classified as "improper ferroelastic." The active representation of the phase transition T-$Na_3ONO_2 \leftrightarrow$TT-$Na_3ONO_2$ is Γ_2^- which corresponds to a "ferroelastoelectric" phase transition. Both phase transitions are allowed to be continuous in Landau theory and in renormalization group theory.

SUMMARY

The investigations described in this paper reveal unique and complex order/disorder phenomena for the nitrite ions in Na_3ONO_2. With decreasing temperature, the orientational disorder of the nitrite ion is reduced by two continuous order processes and one discontinuous phase transition.

In the high-temperature modification (H-Na_3ONO_2) the nitrite ion exhibits a 12-fold orientational disorder. With decreasing temperature (in the temperature range of the M-phase), the disorder is reduced in a continuous order process during which the nitrite ions occupy 2 of the 12 orientations with increasing probability. In their preferred orientations, the nitrite ions form a body-centered tetragonal superstructure while the metric of the M-phase remains cubic within the limits of experimental error.

This continuous order process is interrupted by a discontinuous phase transition at $T = 178$ K, during which the orientational disorder of the nitrite ion is reduced to a two-fold disorder in the T-phase and the body centered tetragonal superstructure of the M-phase is converted to a primitive tetragonal superstructure. The two orientations are occupied with equal probabilities until upon further decrease of the temperature one of them is preferentially occupied in a second continuous order process (TT-phase). In their preferred orientation, the nitrite ions show an anti-ferroelectric alignment of the dipole moments.

The two continuous order processes can both be described by a respective order parameter. These order parameters, which are defined on a microscopic scale, represent the primary order parameters of two continuous phase transitions which accompany the order processes. A more detailed characterization of the phase transitions including theoretical models like the Landau theory or the Potts model (15) would require an exact determination of the critical exponent β. Future experiments will therefore be directed toward measuring additional datapoints, especially in the region of the critical temperatures.

With elastic diffraction techniques it is not possible to distinguish static from dynamic disorder phenomena, because the measured patterns are averaged over space as well as over time. However, solid state NMR measurements on M-Na$_3$ONO$_2$ have shown the disorder to be dynamic. Results of these studies will be published elsewhere.

ACKNOWLEDGMENTS

REFERENCES

1. E. Zintl and M. Morawietz, *Z. Anorg Allg. Chem.* **236,** 372 (1938).
2. M. Jansen, *Angew. Chem.* **88,** 411 (1976).
3. M. Jansen, *Z. Anorg. Allg. Chem.* **435,** 13 (1977).
4. M. Jansen, *Z. Naturforsch.* **37a,** 1457 (1982).
5. J. Kremmler and M. Jansen, dissertation, Kremmler, Hannover, 1987.
6. G. Klösters and M. Jansen, dissertation, Klösters, Bonn, 1997.
7. A. W. Hewatt, *Nucl. Instrum. Methods*, **127,** 361 (1975).
8. A. W. Hewatt and I. Bailey, *Nucl. Instrum. Methods* **137,** 463 (1976).
9. J. Rodriguez-Carvajal, "Program Fullprof," Laboratoire Leon Brillouin, Saclay, France.
10. E. Zintl, A. Harder, and B. Dauth, *Z. Elektrochem.* **40,** 588 (1934).
11. M. I. Kay and B. C. Frazer, *Acta Crystallogr.* **14,** 56 (1961).
12. N. G. Parsonage and L. A. K. Staveley, "Disorder in Crystals." Clarendon, Oxford, 1978.
13. A. D. Bruce and R. A. Cowley, "Structural Phase Transitions." Taylor & Francis, London, 1981.
14. H. T. Stokes and D. M. Hatch, "Isotropy Subgroups of the 230 Crystallographic Space groups." World Scientific, Singapore, 1988.
15. F. Y. Wu, *Rev. Mod. Phys.* **54,** 325 (1982).