160

# Temperature Dependence of Disorder of Nitrite Ions in AgNa(NO₂)₂

By Makoto Ishihara, Shigeru Ohba and Yoshihiko Saito

*Department of Chemistry, Faculty of Science and Technology, Keio University, Hiyoshi 3, Kohoku-ku, Yokohama 223, Japan*

and Yoichi Shiozaki

*Department of Physics, Hokkaido University, Kita-ku, Sapporo 060, Japan*

## Abstract

The crystal structure of $AgNa(NO_2)_2$ in the ferroelectric phase [orthorhombic, $Fd2d$, $Z = 8$, $M_r = 222 \cdot 9$, $\mu = 4 \cdot 375$ mm$^{-1}$, $F(000) = 832 \cdot 8$] has been determined at 118 (1), 218 (1), 268 (1), 297 (1) and 308 (1) K (Mo $K\alpha_1$, $\lambda = 0 \cdot 70930$ Å). That in the paraelectric phase (orthorhombic, $Fddd$, $Z = 8$) has also been examined at 323 (1), 334 (1) and 343 (1) K (Mo $K\alpha$, $\lambda = 0 \cdot 71073$ Å). The $R$ factor is in the range 0·016 to 0·034 for *ca* 300 unique reflections. (I) 118 (1) K: $a = 7 \cdot 607$ (1), $b = 10 \cdot 665$ (1), $c = 10 \cdot 945$ (1) Å, $V = 888 \cdot 0$ (2) Å$^3$, $D_x = 3 \cdot 33$ Mg m$^{-3}$; (II) 218 (1) K: $a = 7 \cdot 728$ (1), $b = 10 \cdot 680$ (1), $c = 10 \cdot 918$ (1) Å, $V = 901 \cdot 1$ (2) Å$^3$, $D_x = 3 \cdot 29$ Mg m$^{-3}$; (III) 268 (1) K: $a = 7 \cdot 830$ (3), $b = 10 \cdot 698$ (1), $c = 10 \cdot 877$ (1) Å, $V = 911 \cdot 1$ (3) Å$^3$, $D_x = 3 \cdot 25$ Mg m$^{-3}$; (IV) 297 (1) K: $a = 7 \cdot 928$ (4), $b = 10 \cdot 717$ (1), $c = 10 \cdot 820$ (2) Å, $V = 919 \cdot 2$ (5) Å$^3$, $D_x = 3 \cdot 22$ Mg m$^{-3}$; (V) 308 (1) K: $a = 8 \cdot 038$ (2), $b = 10 \cdot 742$ (3), $c = 10 \cdot 763$ (2) Å, $V = 929 \cdot 3$ (3) Å$^3$, $D_x = 3 \cdot 19$ Mg m$^{-3}$; (VI) 323 (1) K: $a = 8 \cdot 062$ (1), $b = 10 \cdot 748$ (3), $c = 10 \cdot 754$ (2) Å, $V = 931 \cdot 8$ (3) Å$^3$, $D_x = 3 \cdot 18$ Mg m$^{-3}$; (VII) 334 (1) K: $a = 8 \cdot 077$ (2), $b = 10 \cdot 749$ (3), $c = 10 \cdot 751$ (2) Å, $V = 933 \cdot 3$ (4) Å$^3$, $D_x = 3 \cdot 17$ Mg m$^{-3}$; (VIII) 343 (1) K: $a = 8 \cdot 089$ (1), $b = 10 \cdot 753$ (2), $c = 10 \cdot 744$ (1) Å, $V = 934 \cdot 5$ (2) Å$^3$, $D_x = 3 \cdot 17$ Mg m$^{-3}$. One of the two independent nitrite ions in the ferroelectric phase, $Ag \cdots N{<}^{O}_{O}{:}{:}Na$, exhibits orientational disorder as low as 118 K, whereas the other nitrite ion, $Na \cdots N{<}^{O}_{O}{:}{:}Ag$, is regular below room temperature, suggesting larger covalency in $Ag \cdots O$ bonds than in $Ag \cdots N$. The site dependence of disorder of the nitrite ions corresponds well with the results of Raman spectra. The temperature dependence of the order parameter of the nitrite ions agrees well with that determined by the pyroelectric method. In the paraelectric phase, the populations of two nitrite ions in the environments $Ag{:}{:}^{O}_{O}{>}N \cdots Na$ and $Ag \cdots N{<}^{O}_{O}{:}{:}Na$ are 72 (1) and 28 (1)%, respectively, almost independent of temperature from 323 to 343 K.

## Introduction

Crystals of $AgNa(NO_2)_2$ are ferroelectric with Curie point 311 K (Gesi, 1969). The structures at 293 and 323 K were studied by Ishida & Mitsui (1974) without sufficient analysis of the $NO_2^-$ disorder. The pale yellow color of the crystals is caused by perturbation of $NO_2^-$ by $Ag^+$ ions as in $AgNO_2$ (Yamashita & Azumi, 1984). Structures of $Pb(NO_2)_2.H_2O$ (Ohba, Nosè & Saito, 1985) and $Hg_2(NO_2)_2$ (Ohba, Matsumoto, Ishihara & Saito, 1986) suggested that the post-transition-metal cation in the chelated position between two O atoms of a nitrite ion plays an important role in coloration. On the other hand, there exist not only $Ag^+{:}{:}^{O}_{O}{>}N$ but also $Ag^+ \cdots N{<}^{O}_{O}$ interactions in $AgNO_2$ (Ohba & Saito, 1981), $Ag_2Li(NO_2)_3$ (Ohba, Matsumoto, Ishihara & Saito, 1986) and $AgNa(NO_2)_2$. The temperature dependence of the structure of $AgNa(NO_2)_2$ has been redetermined to see which interaction is stronger and to reveal the nature of the phase transition.

## Experimental

### Data collection

Yellow prisms were grown from $NaNO_2$ aqueous solution saturated with $AgNO_2$. A spherical crystal of diameter 0·32 (5) mm was ground with sandpaper with care against easy cleavage parallel to {101} (Gesi, 1970). Data collection at 118 (1) K (I), 218 (1) K (II), 268 (1) K (III) and 297 (1) K (IV) on a Rigaku AFC-5 four-circle diffractometer with graphite-monochromated Mo $K\alpha_1$ radiation and blowing cold $N_2$ gas evaporated from liquid $N_2$. Data collection at 308 (1) K (V), 323 (1) K (VI), 334 (1) K (VII) and 343 (1) K (VIII) on a Rigaku AFC-4 four-circle

Table 1. *Refinement details*

|  | (I) | (II) | (III) | (IV) | (V) | (VI) | (VII) | (VIII) |
|---|---|---|---|---|---|---|---|---|
| Temperature (K) | 118 (1) | 218 (1) | 268 (1) | 297 (1) | 308 (1) | 323 (1) | 334 (1) | 343 (1) |
| Number of reflections measured | 2800 | 1311 | 1325 | 1532 | 1359 | 1303 | 1304 | 681 |
| Number of reflections observed $[|F_o| > 3\sigma(|F_o|)]$ | 2327 | 1135 | 1091 | 1088 | 1091 | 1068 | 1070 | 557 |
| Number of unique reflections | 637 | 311 | 301 | 302 | 318 | 310 | 319 | 300 |
| $R_{int}$ | 0·012 | 0·013 | 0·013 | 0·014 | 0·026 | 0·024 | 0·025 | 0·019 |
| Number of parameters refined | 41 | 41 | 41 | 41 | 43 | 24 | 24 | 24 |
| $R$ | 0·016 | 0·017 | 0·016 | 0·016 | 0·022 | 0·028 | 0·034 | 0·031 |
| $wR$ | 0·028 | 0·021 | 0·020 | 0·020 | 0·025 | 0·030 | 0·036 | 0·035 |
| $S$ | 1·64 | 1·36 | 1·25 | 1·20 | 1·28 | 1·50 | 1·74 | 1·60 |
| $g$ ($\times 10^4$) | 0·047 (6) | 0·029 (5) | 0·026 (4) | 0·023 (4) | 0·089 (8) | 0·090 (9) | 0·084 (11) | 0·090 (11) |
| $\Delta/\sigma$ | 0·03 | 0·04 | 0·05 | 0·09 | 0·08 | 0·15 | 0·07 | 0·01 |
| $\Delta\rho$ (e Å$^{-3}$) | −1·0–1·5 | −0·5–1·3 | −0·4–1·1 | −0·3–0·8 | −0·8–0·4 | −0·8–0·6 | −0·8–0·8 | −0·8–0·6 |

diffractometer at the Laboratory of Chemistry for Natural Products, Tokyo Institute of Technology, with Mo $K\alpha$ radiation and blowing hot air. Cell parameters refined by least squares for *ca* 20 2$\theta$ values with Mo $K\alpha_1$ (I–IV; 60 < 2$\theta$ < 70°) or Mo $K\alpha$ (V–VIII; 20 < 2$\theta$ < 30°). Experimental details are listed in Table 1. Intensity measurements performed to 2$\theta$ = 80° (I, $h$ −13 → 13, $k$ 0 → 19, $l$ −19 → 19) or to 2$\theta$ = 60° (II, $h$ −10 → 10, $k$ 0 → 15, $l$ −15 → 15; III–VII, $h$ −11 → 11, $k$ 0 → 15, $l$ −15 → 15; VIII, $h$ −11 → 0, $k$ 0 → 15; $l$ −15 → 15), $\theta$–2$\theta$ scan with scan speed 6° min$^{-1}$ in $\theta$ (I–IV) or 4° min$^{-1}$ (V–VIII). No significant variation of five standard reflections. $|F_o|_{max}/|F_o|_{min}$ for 080 and 0,12,0 with $\psi$ scan at 118 K were 1·07 and 1·08, respectively. This may be caused by extinction and absorption. The e.s.d. of $|F_o|$ arising from crystal non-sphericity is 1% (Flack & Vincent, 1978). The difference in reflection conditions between $Fd2d$ and $Fddd$ is for $h0l$ (with $h$ and $l$ even) with or without $h + l = 4n$. Unfortunately, these reflection conditions cannot distinguish the space groups clearly, because all the atoms except O lie on the twofold axis parallel to **b**, which causes pseudo-systematic absences for all-even reflections with $h + k + l = 4n + 2$. Absorption correction ($\mu r = 0·70$, $0·364 \le A \le 0·389$) was made.

## Refinement of the structures

*Paraelectric phase.* The structure (VI) in centro-symmetric space group $Fddd$ was analyzed first to explore the disorder of the nitrite ions. The origin of the coordinates was set on the center of symmetry for convenience of computation. Final coordinates listed in Table 2 were calculated by shifting the origin on the twofold axis for easy comparison with those of $Fd2d$. Atomic coordinates at 323 K reported by Ishida & Mitsui (1974) were utilized as initial parameters. Atomic coordinates and isotropic thermal parameters of Ag, Na, N(11) and O(11) were refined ($R = 0·24$). Then the N(12) and O(12) atoms were introduced with a site-occupation factor, assuming that the sum of the population parameters of the two sites, NO$_2^-$(11) and NO$_2^-$(12), is unity ($R = 0·19$). Reduction of $R$ was achieved by introducing

anisotropic thermal parameters ($R = 0·038$) and an isotropic secondary-extinction-correction parameter, $g$ ($R = 0·027$; Zachariasen, 1967), suggesting large anisotropy of thermal vibration of the Ag atoms as observed in AgNO$_2$ (Ohba & Saito, 1981). At this stage of the refinement, it was revealed that the NO$_2^-$(11) and NO$_2^-$(12) ions are approximately related by a mirror perpendicular to **b** as shown in Fig. 1. The mirror symmetry of the disordered nitrite ions is also observed in NaNO$_2$ (Kay, Gonzalo & Maglic, 1975). The constraint of this mirror symmetry, where the position of the mirror was not fixed and the Ag and Na atoms were assumed regular, reduced
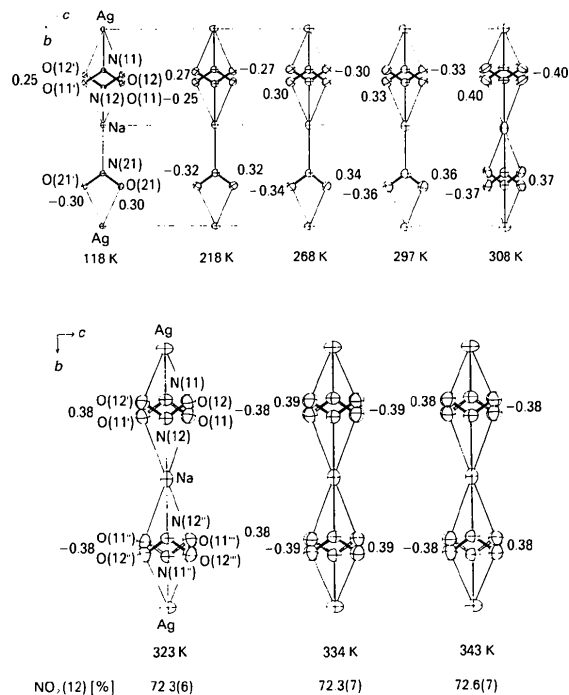


Fig. 1. Temperature dependence of the structures. Two asymmetric units of the ferroelectric phase (upper) and four of that of the paraelectric phase (lower) are projected along **a**. The numbers near the atom labels indicate the distances of the nitrite O atoms from the *bc* plane. Symmetry code: (i) $-x, y, -z$; (ii) $x, 1 - y, -z$; (iii) $-x, 1 - y, z$.

**Table 2. *Positional parameters* ($\times 10^4$) *and equivalent isotropic temperature factors* (Hamilton, 1959)**

| | $x$ | $y$ | $z$ | $B_{eq}$ (Å²×10) |
|---|---|---|---|---|
| **(I)** | | | | |
| Ag | 0 | 0 | 0 | 11(1) |
| Na | 0 | 4881(6) | 0 | 9(1) |
| N11* | 0 | 2099(4) | 0 | 8(1) |
| N12* | 0 | 2956(112) | 0 | 8(1) |
| N21 | 0 | 7327(5) | 0 | 10(1) |
| O11 | −326(3) | 2728(4) | 945(2) | 11(1) |
| O12 | −326(3) | 2327(110) | 945(2) | 11(1) |
| O21 | 397(3) | 7969(3) | 918(2) | 13(1) |
| **(II)** | | | | |
| Ag | 0 | 0 | 0 | 20(1) |
| Na | 0 | 4883(11) | 0 | 15(1) |
| N11* | 0 | 2088(8) | 0 | 15(1) |
| N12* | 0 | 2800(127) | 0 | 15(1) |
| N21 | 0 | 7332(12) | 0 | 17(1) |
| O11 | −351(4) | 2711(6) | 941(3) | 20(1) |
| O12 | −351(4) | 2177(122) | 941(3) | 20(1) |
| O21 | 414(5) | 7969(5) | 914(3) | 23(1) |
| **(III)** | | | | |
| Ag | 0 | 0 | 0 | 27(1) |
| Na | 0 | 4886(11) | 0 | 20(1) |
| N11* | 0 | 2078(7) | 0 | 19(1) |
| N12* | 0 | 2680(48) | 0 | 19(1) |
| N21 | 0 | 7320(9) | 0 | 22(1) |
| O11 | −381(5) | 2694(5) | 937(3) | 28(1) |
| O12 | −381(5) | 2064(45) | 937(3) | 28(1) |
| O21 | 438(5) | 7965(5) | 907(3) | 29(1) |
| **(IV)** | | | | |
| Ag | 0 | 0 | 0 | 33(1) |
| Na | 0 | 4908(15) | 0 | 25(1) |
| N11* | 0 | 2052(7) | 0 | 20(1) |
| N12* | 0 | 2704(28) | 0 | 20(1) |
| N21 | 0 | 7324(13) | 0 | 28(1) |
| O11 | −410(6) | 2672(6) | 933(4) | 31(1) |
| O12 | −410(6) | 2085(22) | 933(4) | 31(1) |
| O21 | 454(5) | 7961(6) | 895(4) | 37(1) |
| **(V)** | | | | |
| Ag | 0 | 0 | 0 | 38(1) |
| Na | 0 | 5016(12) | 0 | 30(1) |
| N11* | 0 | 1983(10) | 0 | 24(2) |
| N12* | 0 | 2609(21) | 0 | 24(2) |
| N21* | 0 | 7263(12) | 0 | 28(2) |
| N22* | 0 | 7875(141) | 0 | 28(2) |
| O11 | −502(10) | 2599(14) | 943(8) | 39(2) |
| O12 | −502(10) | 1994(18) | 943(8) | 39(2) |
| O21 | 454(9) | 7902(10) | 872(6) | 36(2) |
| O22 | 454(9) | 7237(142) | 872(6) | 36(2) |
| **(VI)** | | | | |
| Ag | 0 | 0 | 0 | 41(1) |
| Na | 0 | 5000 | 0 | 31(1) |
| N11* | 0 | 1973(9) | 0 | 29(1) |
| N12* | 0 | 2687(4) | 0 | 29(1) |
| O11 | −474(4) | 2604(7) | 905(3) | 40(1) |
| O12 | −474(4) | 2056(4) | 905(3) | 40(1) |
| **(VII)** | | | | |
| Ag | 0 | 0 | 0 | 42(1) |
| Na | 0 | 5000 | 0 | 32(1) |
| N11* | 0 | 1975(11) | 0 | 31(1) |
| N12* | 0 | 2688(5) | 0 | 31(1) |
| O11 | −478(4) | 2607(8) | 905(3) | 42(1) |
| O12 | −478(4) | 2056(4) | 905(3) | 42(1) |
| **(VIII)** | | | | |
| Ag | 0 | 0 | 0 | 44(1) |
| Na | 0 | 5000 | 0 | 32(1) |
| N11* | 0 | 1969(11) | 0 | 32(1) |
| N12* | 0 | 2685(5) | 0 | 32(1) |
| O11 | −473(5) | 2598(9) | 904(3) | 43(1) |
| O12 | −473(5) | 2056(4) | 904(3) | 43(1) |

* Disordered N atoms.

**Table 2 (cont.)**

Population parameters of the N atoms:

| | (I) | (II) | (III) | (IV) |
|---|---|---|---|---|
| N(11) | 0.974(12) | 0.957(17) | 0.898(11) | 0.733(12) |
| N(12) | 0.026(12) | 0.043(17) | 0.102(11) | 0.267(12) |
| N(21) | 1 | 1 | 1 | 1 |
| N(22) | 0 | 0 | 0 | 0 |

| | (V) | (VI) | (VII) | (VIII) |
|---|---|---|---|---|
| N(11) | 0.496(21) | 0.277(6) | 0.277(7) | 0.274(7) |
| N(12) | 0.504(21) | 0.723(6) | 0.723(7) | 0.726(7) |
| N(21) | 0.952(26) | — | — | — |
| N(22) | 0.048(26) | — | — | — |

the number of parameters from 36 to 24 with no significant change of the $R$ values ($R = 0.028$). In this constraint, the coordinates of the O(12) atom can be written as $(x_{O11}, y_{N11} + y_{N12} - y_{O11}, z_{O11})$. The function $\sum w||F_o| - |F_c||^2$ with $w^{-1} = \sigma^2(|F_o|) + (0.015|F_o|)^2$ was minimized by the full-matrix least-squares program *RADIEL* (Coppens, Guru Row, Leung, Stevens, Becker & Yang, 1979). The smallest extinction factor is 0.64 for 202. Reflection/parameter ratio is 12.9. Final parameters are listed in Table 2 and bond lengths and angles in Table 3. Structures (VII) and (VIII) at 334 and at 343 K were refined in the same manner.*

*Ferroelectric phase.* The atomic parameters at 293 K reported by Ishida & Mitsui (1974) were used as the starting set. The thermal ellipsoids and O—N—O bond angles of the nitrite ions became absurd for (IV) and (V) when the structures of (I) to (V) were refined without considering the disorder of the nitrite ions ($0.016 \le R \le 0.028$). So the split-atom model was adopted for two independent NO₂⁻ ions as described above. Structure (V) was first refined using the atomic parameters of the paraelectric phase (VI). Initial values of the site-occupation factors were NO₂⁻(11): NO₂⁻(12) = 0.15:0.85 and NO₂⁻(21):NO₂⁻(22) = 0.975:0.025. Since the positions of the NO₂⁻ with smaller occupation factors were difficult to determine, the $y$ coordinates of their N atoms were refined after the other parameters had almost converged. This model structure (*b*) is not acceptable in view of the order parameter as described later. When the structure (IV) was refined in the same manner, the site-occupation factor of NO₂⁻(22) became negative, suggesting that there is no disorder for the NO₂⁻(21) ion. To confirm this situation, NO₂⁻(22) was introduced into the final atomic parameters with 0.5% site-occupation factor, which was refined to a negative

Table 3. *Interatomic distances* (Å) *and angles* (°)

Interatomic distances and angles in $NO_2^-(12)$ and $NO_2^-(22)$ are equal to those in $NO_2^-(11)$ and $NO_2^-(21)$ because of the mirror constraint.

|  | (I) | (II) | (III) | (IV) | (V) | (VI) | (VII) | (VIII) |
|---|---|---|---|---|---|---|---|---|
| N(11)–O(11) | 1·258 (4) | 1·254 (6) | 1·249 (6) | 1·251 (7) | 1·277 (12) | 1·246 (4) | 1·248 (5) | 1·244 (5) |
| O(11)–N(11)–O(11i) | 115·5 (4) | 115·9 (7) | 116·3 (6) | 116·0 (7) | 117·6 (11) | 114·1 (4) | 114·0 (5) | 114·1 (5) |
| Ag···N(11) | 2·239 (5) | 2·230 (8) | 2·223 (8) | 2·220 (8) | 2·130 (11) | 2·121 (10) | 2·123 (12) | 2·117 (12) |
| Ag···O(12) | 2·70 (11) | 2·56 (12) | 2·45 (4) | 2·47 (2) | 2·404 (18) | 2·445 (4) | 2·445 (4) | 2·445 (4) |
| Na···N(12) | 2·05 (12) | 2·23 (14) | 2·36 (5) | 2·36 (3) | 2·59 (3) | 2·486 (4) | 2·485 (5) | 2·489 (5) |
| Na···O(11) | 2·530 (7) | 2·552 (12) | 2·574 (11) | 2·621 (16) | 2·817 (18) | 2·779 (7) | 2·777 (8) | 2·786 (9) |
| N(21)–O(21) | 1·253 (4) | 1·249 (8) | 1·252 (7) | 1·238 (9) | 1·218 (10) | — | — | — |
| O(21)–N(21)–O(21i) | 113·7 (4) | 114·0 (10) | 113·1 (8) | 113·1 (11) | 111·5 (11) | — | — | — |
| Ag···O(21) | 2·406 (3) | 2·409 (5) | 2·415 (5) | 2·417 (6) | 2·469 (10) | — | — | — |
| Na···N(21) | 2·609 (8) | 2·615 (17) | 2·604 (15) | 2·589 (21) | 2·414 (18) | — | — | — |
| Ag···N(22) | — | — | — | — | 2·28 (15) | — | — | — |
| Na···O(22) | — | — | — | — | 2·59 (14) | — | — | — |

Symmetry code: (i) $-x, y, -z$.

value. This model structure shown in Fig. 1 gives us a reasonable order parameter. Using these atomic parameters of (IV) as initial values, the structure of (V) was redetermined and then the $NO_2^-(22)$ was introduced. Its site-occupation factor did not become negative and this model structure (a) gave a reasonable order parameter for the nitrites. Structures of (III), (II) and (I) were also refined in the same way using the atomic parameters of the adjacent temperature of measurement. It was confirmed for these structures that the site-occupation factor of $NO_2^-(22)$ became negative when it was refined. The direction of the polar axis was determined based on the anomalous scattering, the difference in the R factor being 0·0004 to 0·0010.* Complex neutral-atom scattering factors were from *International Tables for X-ray Crystallography* (1974). All the calculations were performed on a Facom M-380R of this university.

### Criteria for judging disordered models

We obtained two sets of atomic parameters for (V) by split-atom refinement using different initial parameters. The final site-occupation factors of $NO_2^-(11)$ and $NO_2^-(21)$ are 0·496 (21) and 0·952 (26) for model (a) and 0·148 (41) and 0·687 (18) for model (b). Neither R factors nor Fourier syntheses could justify the final model (a). R factors of (a), (b) and (c) are 0·0224, 0·0222 and 0·0277, respectively, where (c) is an ordered model. There are 39 weak ggg reflections with $h + k + l = 4n + 2$, to which only the nitrite O atoms contribute. R factors for these reflections are 0·173, 0·174 and 0·202, respectively. Fourier synthesis on the $NO_2^-$ plane largely depends on the model. The justification of model (a) was achieved by the order parameter of nitrite ions as described in *Results and discussion*. The order parameters of models (a) and (b) are 0·45 (4) and 0·17 (5), respectively, and that derived from the spontaneous polarization is 0·51 at 308 K (Gesi, 1972). Another shortcoming of model (b) is the unbalanced thermal parameters of the N atoms.

_____

* See deposition footnote.

### Results and discussion

Two asymmetric units of structure in the ferroelectric phase and the corresponding part in the paraelectric phase are shown in Fig. 1. Displacement of the Na atom from the midpoint of a line joining two adjacent Ag atoms on the b axis by ca 0·12 (1) Å gives two sites for the nitrite ions in the ferroelectric phase. The nitrite ions at one of them exhibits 2·6 (12)% disorder at 118 K, whereas those at the other are ordered below room temperature. The difference in temperature dependence of the disorder at two sites corresponds well with the results of Raman spectra (Hangyo & Kato, 1980). At 307 K, just below the Curie point, the peak of the symmetric O–N–O bending vibration splits into four components. The two having higher frequency correspond to the nitrite ions in the Na···N$\overset{O}{\underset{O}{<}}$∴Ag environment and the other two correspond to the nitrite ions in Ag···N$\overset{O}{\underset{O}{<}}$∴Na surroundings. With cooling, one of the N$\overset{O}{\underset{O}{<}}$∴Na bands disappeared faster than that of the N$\overset{O}{\underset{O}{<}}$∴Ag bands (Hangyo & Kato, 1980). The order parameter of the nitrite ion can be written as $S = \frac{1}{2}(S_{11} + S_{21})$, where $S_{11} = 2P(N11) - 1$, $S_{21} = 2P(N21) - 1$ correspond to those for the two independent sites, and $P(N11)$, $P(N21)$ stand for population parameters of the nitrite N atoms. The temperature dependence of $S$ shown in Fig. 2 agrees well with that obtained from observation of the spontaneous polarization by Gesi (1972). The disorder of the nitrite ions is predominantly determined by dipole–dipole interaction between the $Ag^{1/2+}···NO_2^-···Na^{1/2+}$ moieties and secondly by the difference in stabilization energy between Ag···N and Ag$\overset{O}{\underset{O}{::>}}$N interactions. The Ag···N(11) and Ag···O(21) interatomic distances are 2·220 (8) and 2·417 (6) Å, respectively, at 297 K. They are shorter by 0·084 (8) and 0·024 (6) Å, respectively, than those in $AgNO_2$ (Ohba & Saito, 1981), suggesting significant

covalency in these bonds. The ordered arrangement of the $NO_2^-(21)$ ions below room temperature indicates that the N$<^O_O$⋯Ag interaction is stronger than the Ag⋯N bond. The population of nitrite ions in Ag$<^O_O$⋯N configuration is 72·3 (6) to 72·6 (7)% in the paraelectric phase, where the two disordered nitrite ions are located in antiparallel manner along **b**. The previously reported value, *ca* 70%, roughly
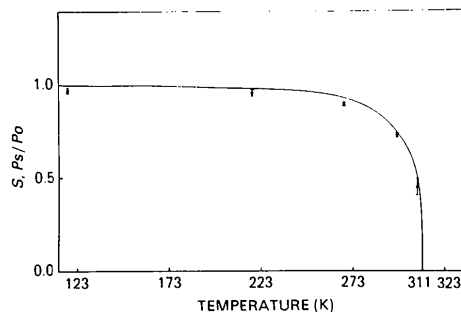


Fig. 2. The temperature dependence of the order parameter. The solid line shows the values observed by Gesi (1972). Points with error bars represent the values of the present work.
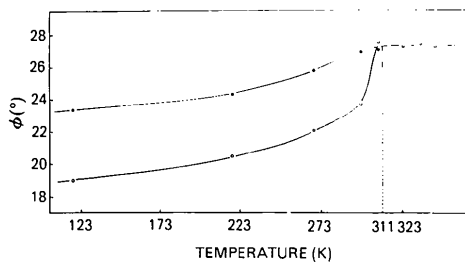


Fig. 3. The temperature dependence of the inclination angles of the NO₂ plane to the *bc* plane. The upper curve is for $NO_2^-(21)$ and the lower for $NO_2^-(11)$.

estimated by Ishida & Mitsui (1974), was confirmed. Although the value of the population is practically independent of temperature from 323 to 343 K, it is expected to decrease at higher temperature. However, the reported decomposition temperature is 353 K (Gesi, 1970). The inclination angle $\varphi$ of the $NO_2^-$ plane to the *yz* plane increases with temperature in the ferroelectric phase and remains almost constant in the paraelectric phase as shown in Fig. 3. The increase in lattice constant *a* and the decrease in *c* with temperature in the ferroelectric phase are mainly due to the increase in angle $\varphi$ with the relation $\Delta c / \Delta a \simeq -\tan \varphi$.

**References**

COPPENS, P., GURU ROW, T. N., LEUNG, P., STEVENS, E. D., BECKER, P. J. & YANG, Y. W. (1979). *Acta Cryst.* A35, 63–72.
FLACK, H. D. & VINCENT, M. G. (1978). *Acta Cryst.* A34, 489–491.
GESI, K. (1969). *J. Phys. Soc. Jpn*, 26, 1554.
GESI, K. (1970). *J. Phys. Soc. Jpn*, 28, 395–401.
GESI, K. (1972). *J. Phys. Soc. Jpn*, 33, 108–111.
HAMILTON, W. C. (1959). *Acta Cryst.* 12, 609–610.
HANGYO, M. & KATO, R. (1980). *J. Phys. Soc. Jpn*, 48, 1209–1218.
*International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
ISHIDA, K. & MITSUI, T. (1974). *Ferroelectrics*, 8, 475–476.
KAY, M. I., GONZALO, J. A. & MAGLIC, R. (1975). *Ferroelectrics*, 9, 179–186.
OHBA, S., MATSUMOTO, F., ISHIHARA, M. & SAITO, Y. (1986). *Acta Cryst.* C42, 1–4.
OHBA, S., NOSÉ, Y. & SAITO, Y. (1985). *Acta Cryst.* C41, 1385–1388.
OHBA, S. & SAITO, Y. (1981). *Acta Cryst.* B37, 1911–1913.
YAMASHITA, A. & AZUMI, T. (1984). *J. Phys. Chem.* 88, 4622–4626.
ZACHARIASEN, W. H. (1967). *Acta Cryst.* 23, 558–564.