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X-ray study of deformation density and spontaneous polarization in ferroelectric $NaNO_2$

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The deformation electron density of ferroelectric sodium nitrite has been determined from X-ray diffraction data at 30 K, using Hirshfeld deformation functions. Owing to the strong correlation between odd terms of the deformation coefficients, constraints were imposed in the refinement. The net charges for Na, N and O atoms were estimated to be 0.27, 0.20 and −0.24 e, respectively. The calculated spontaneous polarization using these net charges and atomic dipole terms, 7.8 $\mu C\,cm^{-2}$, is much closer to the recently measured value, 12 $\mu C\,cm^{-2}$, as compared with the value calculated from the formal point charges (74 $\mu C\,cm^{-2}$).

1. Introduction

Since the discovery of its ferroelectricity (Sawada *et al.*, 1958), sodium nitrite ($NaNO_2$) has been extensively investigated. It is one of the typical order–disorder ferroelectrics with the simplest structure (Kay & Frazer, 1961), as shown in Fig. 1. Although many properties of $NaNO_2$ have been characterized, there are some unsolved problems. One of them is the discrepancy between the calculated and observed spontaneous polarization (P_s). The P_s value calculated by Kay & Frazer (1961), using the results of their neutron structure analysis and with formal point charges (Na^+, N^{3+} and O^{2-}), is 74 $\mu C\,cm^{-2}$. This is quite different from the recently measured values of 11.9 $\mu C\,cm^{-2}$ by Hamano (1973) and 11.7 $\mu C\,cm^{-2}$ by Buchheit & Petersson (1980). The formal point charge model is clearly too crude to reflect the actual charge distribution in the crystals.

Spontaneous polarization is one of the most important physical properties of ferroelectrics, and originates from the details in the charge distribution in the crystals. Experimental information about electron density is mainly obtained from X-ray diffraction studies of single crystals. The deformation density includes important features such as bonding and lone-pair electrons, but is very small compared with the total electron density. Different methods have been used for analysis of the deformation density (see, for example, Jeffrey & Piniella, 1991). Okuda *et al.* (1990) analyzed the electron density of $NaNO_2$ at 120 K using the deformation model proposed by Hansen & Coppens (1978). They reported the deformation density for the NO_2^- ion and the net charges for N (−0.18 e) and O (−0.41 e). They fixed, however, the charge of Na to +1 e, and did not discuss its ferroelectricity.

A detailed study of a simple structure such as $NaNO_2$ may provide valuable fundamental information about ferroelectricity and form the groundwork for understanding more complicated materials. Therefore, as the first step to obtaining microscopic information about ferroelectric crystals by X-ray diffraction, we have attempted to analyze the deformation electron density of $NaNO_2$ by Hirshfeld deformation functions (Hirshfeld, 1971, 1977), estimated the net charges including the Na atom and then derived the P_s value, to compare with the value from formal point charges.

2. Experimental

Single crystals of $NaNO_2$ were grown from aqueous solution at room temperature. A prismatic crystal with (010) basal plane was used as the specimen; boundary planes (101), $(\bar{1}0\bar{1})$, $(\bar{1}01)$, $(10\bar{1})$, (010), $(0\bar{1}0)$, (001), $(00\bar{1})$; volume 5.43×10^{-3} mm^3. Most experimental details are given in Table 1. The diffractometer was equipped with a 400 mm χ-circle and a two-stage closed-cycle helium refrigerator (Samson *et al.*, 1980). The lowest available temperature, 30 K, was chosen in order to avoid severe correlations between displacement and deformation parameters. The scan step width was 0.01° in ω with a minimum number of 70 steps plus $\alpha_1 - \alpha_2$ splitting. The measuring time varied from 0.3 to 3.0 s step^{-1}. Five standard reflections, $12\bar{3}$, $1\bar{1}0$, $00\bar{2}$, $\bar{2}0\bar{2}$ and $\bar{1}10$, were monitored over 104 h of total X-ray exposure time. The intensities and corresponding standard deviations were corrected for time variations by the method of McCandlish *et al.* (1975).

3. Analysis and results

In the weighting scheme $\sigma^2(F_o{}^2)$ was estimated from counting statistics and the scatter of the standard reflections. Six low-order reflections ($10\bar{1}$, $\bar{1}0\bar{1}$, 200, $\bar{2}00$, 020, $0\bar{2}0$) were excluded from the refinement because of severe extinction. All the other 1390 reflections measured in half of the reciprocal sphere were used in the least-squares refinement without averaging. The most severely extinction-corrected reflections are $\{12\bar{1}\}$ with $y = 0.89$.

In the first steps, a spherical-atom model refinement was performed. The atomic coordinates from the 295 K data refinement (Gohda *et al.*, 1996) were utilized as starting

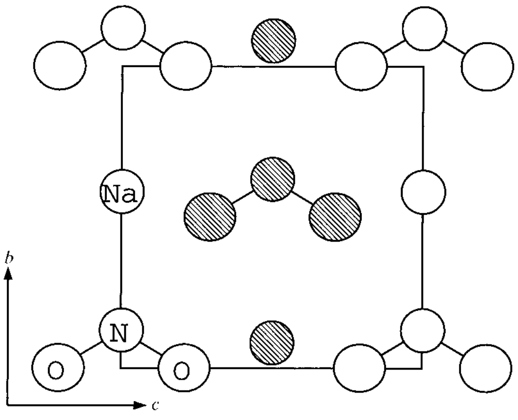

Figure 1
Crystal structure of $NaNO_2$ in the ferroelectric phase projected along the *a* axis. The shaded atoms are in the $x = \pm 1/2$ plane.

Table 1
Experimental details.

Crystal data	
Chemical formula	$NaNO_2$
Chemical formula weight	69.0
Cell setting	Orthorhombic
Space group	*Im2m*
a (Å)	3.5024 (6)
b (Å)	5.5209 (5)
c (Å)	5.3789 (9)
V (Å^3)	104.007 (16)
Z	2
D_x (Mg m^{-3})	2.203
Radiation type for cell parameter determination	Mo $K\alpha_1$
Wavelength (Å)	0.70930
No. of reflections for cell parameters	15
θ range (°)	26.378–27.414
μ (mm^{-1})	0.3853
Temperature (K)	30
Crystal form	Hexagonal prism
Crystal size (mm)	$0.223 \times 0.180 \times 0.075$
Crystal colour	Colourless
Data collection	
Diffractometer	HUBER/Stoe/ARACOR
Data collection method	$\omega/2\theta$ scans
Radiation type for data collection	Mo $K\alpha$
Wavelength (Å)	0.7103
Absorption correction	Integration (*ABSSTOE*; Lundgren, 1983)
$T_{\min}$	0.9228
$T_{\max}$	0.9475
No. of measured reflections	1396
No. of independent reflections	384
No. of observed reflections	384
Criterion for observed reflections	$I > -3\sigma(I)$
$R_{\rm int}$	0.012
$\theta_{\max}$ (°)	52.989
Range of h, k, l	$-7 \rightarrow h \rightarrow 7$ $-12 \rightarrow k \rightarrow 12$ $-12 \rightarrow l \rightarrow 0$
No. of standard reflections	5
Frequency of standard reflections	Every 240 min
Intensity decay (%)	0.06
Refinement	
Refinement on	F^2
$R(F)$	0.0084
$wR(F^2)$	0.0215
S	1.7937
No. of reflections used in refinement	1390
No. of parameters used	68
Weighting scheme	$w = 1/\sigma^2(F^2)$
$(\Delta/\sigma)_{\max}$	0.0305
$\Delta\rho_{\max}$ (e Å^{-3})	0.11
$\Delta\rho_{\min}$ (e Å^{-3})	−0.12
Extinction method	Becker & Coppens (1975) type 1 Lorentzian isotropic
Extinction coefficient	$0.177 (7) \times 10^4$
Source of atomic scattering factors	*International Tables for X-ray Crystallography* (1989, Vol. IV)
Computer programs	
Data collection	*DIF*4
Cell refinement	*LATCON* (Lundgren, 1983)
Data reduction	*STOEDATRED* (Lundgren, 1983)
Structure refinement	*DUPALS* (Lundgren, 1983)

Table 2
Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2).

$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^ia^j\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	$U_{\rm eq}$
Na	0	0.58833 (4)	0	0.00573 (3)
N	0	0.12277 (4)	0	0.00595 (4)
O	0	0	0.19646 (3)	0.00685 (4)

Table 3
Anisotropic displacement parameters (Å^2).

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Na	0.00623 (3)	0.00538 (3)	0.00559 (3)	0	0	0
N	0.00836 (4)	0.00461 (5)	0.00490 (4)	0	0	0
O	0.00886 (4)	0.00706 (5)	0.00462 (4)	0	0	0.00076 (4)

Table 4
Selected geometric parameters (Å^2, °).

Na—N	2.5703 (3)	Na—O$^{\rm ii}$	2.4434 (3)
Na—O$^{\rm i}$	2.5064 (2)	N—O	1.2554 (1)
O—N—O$^{\rm iii}$	114.65 (1)		

Symmetry codes: (i) $x, 1+y, z$; (ii) $x-\frac{1}{2}, \frac{1}{2}+y, z-\frac{1}{2}$; (iii) $x, y, -z$.

parameters. The refined parameters were one scale factor, one isotropic extinction coefficient, three atomic coordinates and ten anisotropic displacement parameters. The discrepancy factors after this series of refinement were $R(F^2) = 0.0260$, $wR(F^2) = 0.0382$, $S = 3.12$.

Deformation density functions proposed by Hirshfeld (1977) were subsequently introduced in the refinement. The static electron density of each atom ρ_i is here expressed by a neutral spherical atom density $\rho_i^{\rm sph}$, plus a deformation density expressed as a linear combination of deformation functions,

$$\rho_i = \rho_i^{\rm sph} + \sum_{n,k} c_{i,n,k}\delta\rho_{i,n,k},$$

where $c_{i,n,k}$ are refinable deformation coefficients. The deformation functions $\delta\rho_{i,n,k}$ have the general form

$$\delta\rho_{i,n,k} = N_n r_i^{\,n}\exp(-\gamma_i r_i^{\,2})\cos^n\theta_k,$$

where N_n is a normalization factor, n is an integer from 0 to 4, r_i is the distance from the atom centre, γ_i is a parameter which governs the radial breadth of the deformation functions on each type of atom, and θ_k is the angle between radius vector r_i and a specified polar axis k. The normalizing factors of even terms are chosen to make the volume integral of each function equal to one electron. The sum of the even coefficients therefore represents the net charge of the atom. The normalizing factors of odd terms are defined to make the integral over the half space bounded by the plane $\theta_k = \pi/2$ equal to half an electron. The odd coefficients therefore express an intra-atomic dipole moment. The number of polar axes k is $(n+1)(n+2)/2$, so the maximum number of deformation coefficients is 35 per atom. In the case of $NaNO_2$ the number of independent deformation coefficients is reduced to 14, 14 and 22 for Na, N and O, respectively, due to symmetry restrictions.

Deformation coefficients were released successively, starting from the lower terms, together with the structural parameters. However, the correlations between odd terms of deformation coefficients were quite strong, so that we could not release all parameters simultaneously. We imposed the following least constraints in order to reduce the number of independent deformation coefficients:

(i) A mirror plane including the N—O bond and normal to the *b*–*c* plane was introduced for the deformation coefficients of the O atom (Fig. 1). Under this constraint, sodium, nitrogen and mirror-constrained oxygen deformation coefficients were refined.

(ii) After all the parameters above were refined, the constraint was released. All the parameters of the O atoms were refined, keeping sodium and nitrogen deformation coefficients fixed in the final three cycles of refinement.

The optimization of γ_i was performed after the above procedure by finding the minimum of the goodness-of-fit, S, when changing γ_i in steps of 0.5, resulting in 3.0, 6.0 and 7.5 for sodium, nitrogen and oxygen, respectively. Finally, the net charges +0.27, +0.20 and −0.24 e for Na, N and O, respectively, were obtained. Atomic fractional coordinates, anisotropic displacement parameters and geometric parameters are listed in Tables 2, 3 and 4, respectively.[1]

Some of the dynamic deformation densities and the final residual densities are shown in Figs. 2 and 3, respectively. The discrepancy factors are listed in Table 1.

The spontaneous polarization, P_s, was calculated from the expression

$$P_s = \frac{\sum(\Delta Y_i q_i + \mu_i)}{V},$$

where q_i is the net charge, V is the volume of the unit cell and μ_i is the atomic dipole moment, calculated from the odd deformation coefficients. ΔY_i means half of the atomic displacement which occurs on switching the polarization direction. In order to obtain ΔY_i we require information about the structure of the paraelectric phase, because ΔY_i cannot be obtained only from the structure of the ferroelectric phase. The y coordinate of the mirror plane perpendicular to the b axis, which appears in the paraelectric phase, was assumed to be the same as the fixed point of the polarization reversal and this y coordinate was taken from that of Komatsu *et al.* (1988). The calculated P_s value of 7.8 μC cm^{-2} is much nearer to the observed values given in Table 5 than the value calculated from formal charges (Kay & Frazer, 1961).

Finally we must note the differences between the present result and the result reported at the 9th International Meeting on Ferroelectricity (Gohda *et al.*, 1998), abbreviated to IMF9. In the present paper we report a P_s value of 7.8 μC cm^{-2}

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[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS0030). Services for accessing these data are described at the back of the journal.

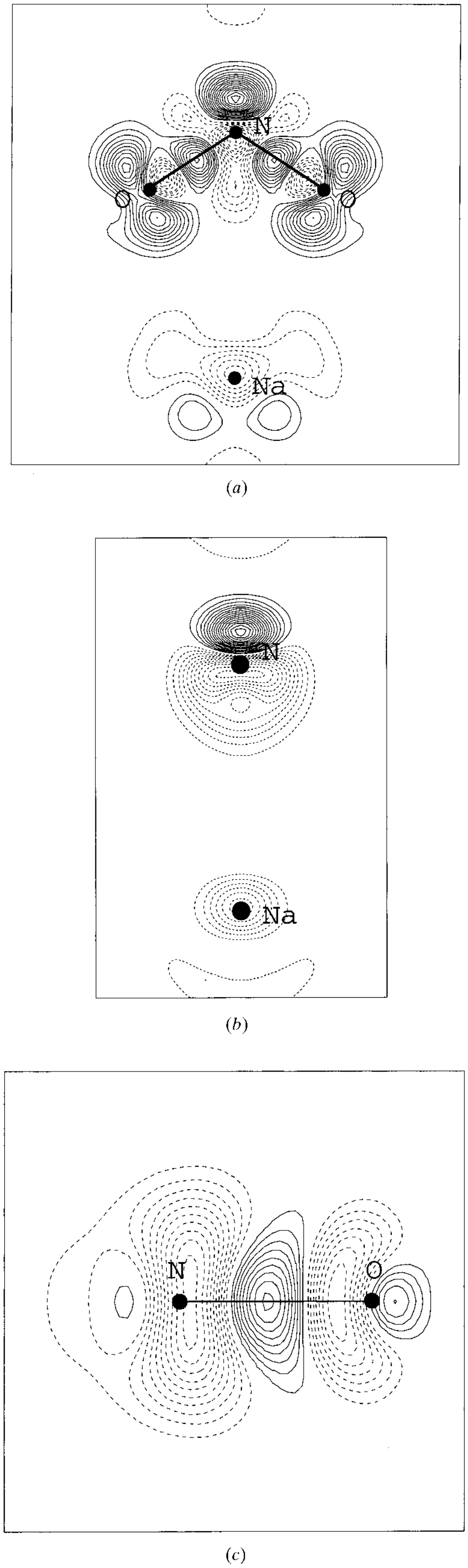


Figure 2
Deformation density (*a*) in the *b*–*c* plane at $x = 0.5$, (*b*) in the *a*–*b* plane at $z = 0.5$ and (*c*) in the plane containing the N—O bond axis and perpendicular to the NO_2 plane. Contour intervals are shown at 0.05 e Å^{-3}.

Table 5
Observed spontaneous polarization.

Value (μC cm^{-2})	Comment	Reference
8–10	Estimated from figure	Sawada *et al.* (1961)
8.6	Room temperature	Nomura (1961)
11.9	Estimated saturated value	Hamano (1973)
11.7	Estimated saturated value	Buchheit & Petersson (1980)

whereas, at IMF9, 7.3 μC cm^{-2} was reported. This discrepancy is due to the lack of strict charge neutrality in the net charges refined by least-squares methods. The former value corresponds to twice the value summed up over a formula unit with *y* coordinates close to each other, *i.e.* $2(q_{\rm Na}y_{\rm Na} + \ldots)b/V$. The latter is the value calculated by the summation over the unit cell, *i.e.* $[q_{\rm Na}(y_{\rm Na} + y_{\rm Na} + 1/2) + \ldots]b/V$. If charge neutrality is strictly satisfied, the above two expressions give the same value. At IMF9 we reported a maximum peak height in the residual density of 0.25 e Å^{-3}, whereas in the present paper we report a value of 0.11 e Å^{-3}. This is because six low-order reflections with strong extinction were excluded in the present refinement and differential Fourier syntheses. This results in the smaller maximum peak height.

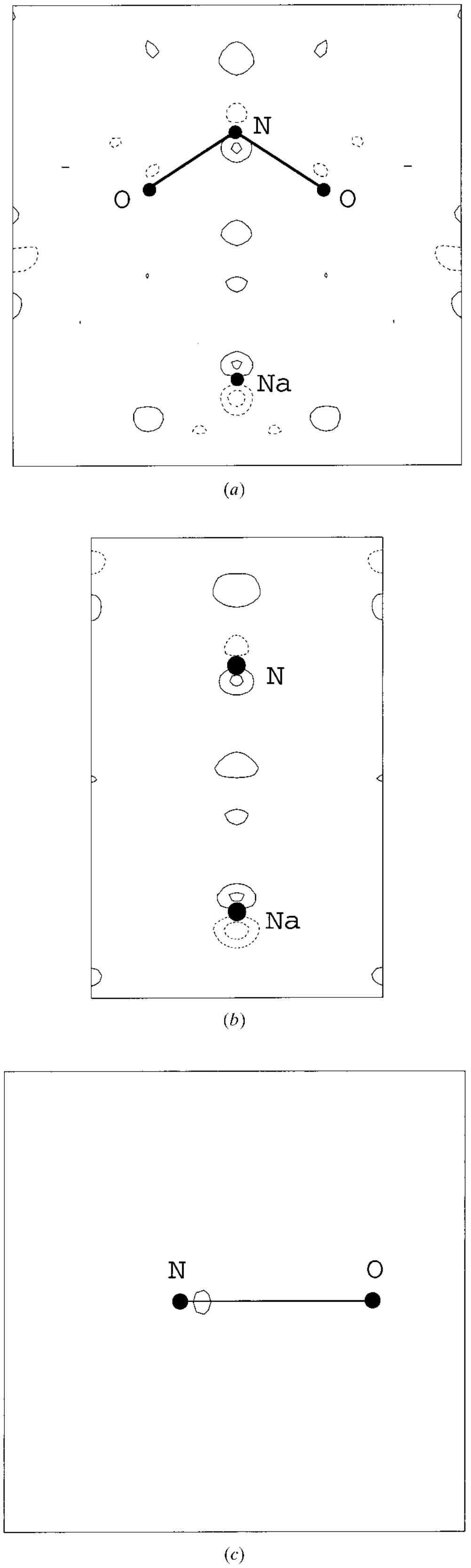
4. Discussion

As described above, we could obtain a satisfactory P_s value from Hirshfeld deformation-density analysis, close to the observed P_s values from dielectric measurements. However, the following points should be noted.

The problem of this analysis is that a perfect convergence of the least-squares refinement (*i.e.* convergence when releasing all refinable parameters simultaneously) has not been attained. However, the final discrepancy factors $[R(F) = 0.84\%]$ became acceptably small. Our deformation density around the NO_2^- ion is similar to that of Okuda *et al.* (1990) and that of Kikkawa *et al.* (1987) calculated by *ab initio* molecular-orbital methods. Moreover, the residual maps (Fig. 3) are featureless and the maximum peak height is 0.11 e Å^{-3}. Thus, the bias of our constraint does not seem severe.

Gesi (1969) reported a phase transition in $NaNO_2$ at 178 K. Also, Ema *et al.* (1975) found a small anomaly in the thermal expansion coefficient at 173 K. In order to detect any change in the space group below 173 K, the low-angle part of the data ($2\theta \leq 30^\circ$) was collected with the primitive cell at 30 K. In our data set, no reflection was found to break the extinction rule of the body-centred lattice ($h + k + l$ = odd). Moreover, no anomaly was found in the discrepancy factors and displacement parameters when the space group *Im*2*m* was used. Thus, the space group *Im*2*m* seems to be valid at 30 K from a diffraction point of view.

The major difference between Okuda *et al.* (1990) and the present work is the expression for the anisotropy of the electron density. We used Hirshfeld's deformation functions



(*a*)

(*b*)

(*c*)

Figure 3
Final residual density (*a*) in the *b*–*c* plane at $x = 0.5$, (*b*) in the *a*–*b* plane at $z = 0.5$ and (*c*) in the plane containing the N—O bond axis and perpendicular to the NO_2 plane. Contour intervals are shown at 0.05 e Å^{-3}.

Table 6
Reported net charges of sodium from some earlier X-ray studies.

Material	Charge of Na (e)	Reference
NaSCN	0.27	Bats *et al.* (1977)
NaSCN	0.11	Coppens *et al.* (1979)
$H_2NC_6H_4SO_3Na.2H_2O$	0.07	Bats (1977*b*)
$NaCN.2H_2O$	0.10	Bats (1977*a*)
$Na_2S_2O_3$	0.77	Bats & Fuess (1986)
NaF	0.95	Su & Coppens (1995)
NaH_2PO_4	0.20	Ichikawa *et al.* (1998)

(involving $\cos^n \theta$) while they used spherical harmonics proposed by Hansen & Coppens (1978). One interesting point is whether the difficulty in convergence is due to the choice of the deformation functions.

Our net charges obtained are close to neutral as compared with the formal charges. Table 6 shows the values of the net charges for sodium obtained in earlier X-ray studies. In general, the charge +1 e of alkaline metals seems to be adopted. Su & Coppens (1995) reported a net charge of +0.95 e for Na in NaF. On the other hand, a charge of 0.20 e for Na was obtained with Hirshfeld's deformation functions in NaH_2PO_4 (Ichikawa *et al.*, 1998). Bats & Fuess (1986) pointed out that the net charges of the alkaline cations are not well defined and reported various net charges of Na in $Na_2S_2O_3$ depending on the method. Therefore, it may be necessary to treat the same data by a different procedure (*e.g.* multipole refinement) as well as to apply the Hirshfeld method to other literature data.

Finally, it is noted that Resta (1994*a*,*b*) states that the spontaneous polarization has nothing to do with the periodic charge density of the polarized crystal. In our calculation of P_s we used not only the charge density (the net charge and atomic dipole) in the ferroelectric phase, but also knowledge of the structure of the paraelectric phase. However, the limitation of applicability in our approach remains to be clarified.

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