On the local motions in ferroelectric NaNO$_2$ from $^{23}$Na NMR data

Mrignayani Kotecha $^{a}$, Lakshman Pandey $^{a}$

$^{a}$ Department of Physics, Rani Durgavati University, Jabalpur, India

First Published on: 01 January 2001
To cite this Article: Kotecha, Mrignayani and Pandey, Lakshman (2001) 'On the local motions in ferroelectric NaNO$_2$ from $^{23}$Na NMR data', Ferroelectrics, 249:1, 197 - 206
To link to this article: DOI: 10.1080/00150190108225996
URL: http://dx.doi.org/10.1080/00150190108225996
ON THE LOCAL MOTIONS IN FERROELECTRIC 
NaNO₂ FROM \( ^{23}Na \) NMR DATA 

MRIGNAYANI KOTECHA and LAKSHMAN PANDEY* 

Department of Physics, Rani Durgavati University, Jabalpur - 482001, India 

(Received July 30, 1999; In final form March 30, 2000) 

Electric field gradients (efg) at the sites of sodium in the ferroelectric NaNO₂ are calculated for various local motions. It is found that the values of efg obtained from \( ^{23}Na \) NMR data are best represented when the NO₂ groups are considered to be executing flipping motion by 170° about an axis whose direction cosines are 0.99, 0.11, 0.06 with respect to the crystal axes (c, a, b). Such a motion is in conformation with the not-so-widely known fact that the electric polarization in ferroelectric NaNO₂ has a spiraling orientation as one moves from one domain to the other. 

Keywords: NaNO₂; EFG; NMR of Ferroelectric NaNO₂; Ferroelectric Domain; M- Tensor 

AIP’s PACS Codes: 77.80 Dj; 76.60 Es; 77.80 Gv; 33.25 +k; 77.84 Bw 

INTRODUCTION 

Sodium nitrite is a typical order-disorder ferroelectric, which undergoes a transition first to a sinusoidal anti-ferroelectric phase at 437K and then to a paraelectric phase at 438K [1–4]. The permanent electric dipole moment of NO₂ group is responsible for ferroelectricity in this material, and at low temperatures the NO₂ groups are aligned in the bc plane of the orthorhombic unit cell shown in Figure 1[5], with their electric dipole moments pointing along one direction of the ferroelectric b axis. The transition from the ferroelectric phase occurs by progressive reversal of the orientation of the NO₂ groups, so that, in the paraelectric phase their dipole moments are oriented with equal probability along the two directions of b axis. A normal NaNO₂ crystal has arrangements of alternate 180° domains separated by the so-called domain-walls [3,4,6,7]. The structure of domain-walls has been studied by several workers [7,8]. It was shown by Hughes 

* Corresponding Author. E-mail: pandeyl@hotmail.com
and Pandey [9] from NMR line-shape studies that the electric polarization has a spiral orientation, like Bloch walls, as one moves from one domain to the adjacent 180° domain. Also, it was deduced by them from the 23Na spin-lattice relaxation measurements that the NO2 groups are undergoing sudden reorientations probably about the crystal a-axis normal to the plane of NO2 groups[10].

![Unit cell of NaNO2 and the coordinate systems used to specify the direction of magnetic field](image)

**FIGURE 1** Unit cell of NaNO2 and the coordinate systems used to specify the direction of magnetic field

The dynamical model of flipping NO2 groups successfully explains the 23Na spin-lattice relaxation results at temperatures ranging from 437K, the transition temperature, down to 220K [10]. In this temperature range, the spin-lattice relaxation of 23Na is predominantly quadrupolar [11,12], as established by Hughes and coworkers [13–15]. It means that the spin energy is transferred to the lattice through the interaction between the nuclear quadrupole moment and the fluctuating electric field gradient (efg) at the site of 23Na. However, the values of the components of the efg tensor (in fact quantities involving product of these and generally known as M-tensor components) calculated by them using point charge model and different internal motions do not show very satisfactory agreement with their experimental results [14,15].

Models for local dynamics have been proposed by various workers to explain the thermal expansion behaviour [16], results of neutron scattering studies [17], I. R. absorption [18], Raman experiments [19], 14N and 23Na NMR results [20–
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24], ESR studies on NO₂ radicals [22–25], X-ray topographic study of domain walls [23,26], study of dispersion behaviour [27] and dielectric relaxation [28]. It has been generally agreed that the reorientational motions of the NO₂ groups probably about a or c axes and a very small displacement of 'Na' ion play the most important role. But to the best of our knowledge, the local motions that represent the NMR data best have not been understood clearly. As NMR of quadrupolar nuclei is a very sensitive probe for the study of local environment in a material, models representing the NMR data best would be most close to the real dynamic situations.

Our purpose in this paper is to calculate the $\mathbf{M}$-tensor components mentioned above by visualizing different possible movements and to point out the local motions in NaN0₂ that represent the NMR result best. A preliminary report of this was presented earlier [29].

The next section gives, in brief, the crystallographic information about NaN0₂, followed by calculation of $\mathbf{M}$-tensor components. The calculated results are compared with the experimental values afterwards, followed by conclusion.

CRYSTALLOGRAPHIC INFORMATION ABOUT NaN0₂

The crystal structure of NaN0₂ is well established [5,30] and is given here for a ready reference. As shown in Figure 1, the unit cell has two molecules with the same point symmetry. The lattice belongs to the Non-Centrosymmetrical body centered orthorhombic system with the space groups $\text{C}_{2h}^{20} - \text{Im}
\text{2m}$. The dimensions of the cell are $a_0 = 3.560 + 0.010 \text{Å}$, $b_0 = 5.60 + 0.005 \text{Å}$, and $c_0 = 5.384 + 0.005 \text{Å}$ at room temperature. The position of atoms in the unit cell is [30],

\[
\begin{align*}
2\text{N}: & \quad (0, 0, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}) & \quad + & \quad (0, t, 0) \\
2\text{Na}: & \quad + & \quad (0, w, 0) \\
4\text{O}: & \quad + & \quad (0, u, v; 0, u, -v)
\end{align*}
\]

The values of the atomic coordinates in fraction of unit cell dimensions are $t = 0.1200 + 0.0007$, $w = 0.5853 + 0.0010$, $u = 0.0000$ and $v = 0.1941 + 0.0006$ at room temperature.

The phase transition occurs at about 437K and the lattice transforms to the Centro-symmetrical body-centered orthorhombic system with the space group $\text{D}_{2h}^{25} - \text{Im}
\text{m}
\text{m}$. 
CALCULATION OF M-TENSOR COMPONENTS FROM $^{23}$Na NMR DATA

We give here in brief, for the sake of clarity and completeness the methodology for obtaining the values of M-tensor components from NMR data. The $^{23}$Na (I = 3/2) NMR spectrum obtained from a single crystal of NaNO$_2$ is a well-resolved quadrupole split triplet. At temperatures above 270K, the $^{23}$Na nuclei relax primarily via the quadrupole transitions $m = \pm 3/2 \leftrightarrow \pm 1/2$ and $m = \pm 3/2 \leftrightarrow \mp 1/2$ with probabilities $W_1$ and $W_2$ [14,15, 30–34], respectively, which vary quite strongly with the orientation of the crystal relative to the external magnetic field [14,15].

For a system of I = 3/2 nuclei situated at identical sites in a single crystal and relaxing via a direct quadrupole relaxation process, the probability $W_1$, can be written as [10]

$$W_1 = \frac{e^2 Q^2/12}{\hbar^2} \int_{-\infty}^{+\infty} \left[ V_{\alpha\beta}(t) + iV_{\alpha'\beta'}(t) \right] \left[ V_{\alpha\beta}(t + \tau) + iV_{\alpha'\beta'}(t + \tau) \right] e^{-i\omega\tau} d\tau$$

(1)

where $eQ$ is the nuclear quadrupole moment, $\omega$ is the frequency of the $\Delta m = \pm 1$ transitions involved and $V_{\alpha\beta}(t)$ and $V_{\alpha'\beta'}(t)$ are time-dependent components of the electric field gradient tensors at the nuclear sites in a coordinate system whose $z$ axis is parallel to the magnetic field.

The right hand side of Eq. (1) involves factors that are products of $V_{\alpha\beta}(t)$ and $V_{\alpha'\beta'}(t)$. These are the components of the so-called M-tensor and are given by [34]

$$M_{\alpha\beta\alpha'\beta'} = \frac{2\pi}{\hbar} \sum_{nn'} \exp(-E_n/kT) \langle n'|V_{\alpha\beta}|n\rangle \langle n'|V_{\alpha'\beta'}|n\rangle \times \delta(E_{n'} - E_n + E_{m+\mu} - E_m) \left( \sum_{nn'} \exp(-E_n/kT) \right)^{-1}$$

(2)

where $\alpha, \beta, \alpha', \beta' = 1, 2$ and 3 for $x, y$ and $z$, $T$ is the temperature, $V_{\alpha\beta}$ is $\partial^2 V/\partial x_{\alpha} \partial x_{\beta}$, $E_n$ and $E_m$ are eigen values of the lattice and spin system, $n$ and $n'$ are initial and final lattice states and $m$ is 1 and 2 for $W_1$ and $W_2$ respectively. Explicit expressions involving the orientation dependence have been derived by Hughes and coworkers for various symmetries of the lattice [15,34]. Experimental determination of $W_1$ (or $W_2$) as a function of orientation of the external field with respect to the principal axis system directly yields the values of $M_{\alpha\beta\alpha'\beta'}$. Hughes and coworkers [14,15,34] have done considerable amount of work on
this and the values of $M$-tensor components obtained by them experimentally by measuring the orientation dependence of $W_1$ are given in Table I, at temperatures of our interest.

Table I: Ratios of $M$-tensor Components of $^{23}$Na in NaN$_2$. The numbers 1, 2 and 3 correspond to $x$, $y$, and $z$ respectively.

<table>
<thead>
<tr>
<th>$M$-tensor Ratios</th>
<th>Experimental Values</th>
<th>Theoretical values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>235K</td>
<td>298K</td>
</tr>
<tr>
<td>$M_{1111}/M_{3333}$</td>
<td>0.79</td>
<td>0.74</td>
</tr>
<tr>
<td>$M_{1333}/M_{3333}$</td>
<td>-0.73</td>
<td>-0.68</td>
</tr>
<tr>
<td>$M_{3233}/M_{3333}$</td>
<td>0.05</td>
<td>0.06</td>
</tr>
<tr>
<td>$M_{3131}/M_{3333}$</td>
<td>0.16</td>
<td>0.16</td>
</tr>
<tr>
<td>$M_{1212}/M_{3333}$</td>
<td>0.11</td>
<td>0.13</td>
</tr>
</tbody>
</table>

a. Flipping motion of dipoles situated at the six nearest NO$_2$ sites by $\theta \approx 85^\circ$ and $\phi \approx 25^\circ$.
b. Flipping motion of six nearest NO$_2$ groups by $170^\circ$ about the axis whose direction cosines are $0.99, 0.11, 0.06$ with Na displacement of about $0.005\AA$ in b axis.

VALUES OF $M_{\alpha\beta}\alpha'\beta'$. USING DIPOLE MOMENT OF NO$_2$ AND POINT CHARGES

We make an attempt to understand the local motions taking place inside the crystal such that the $M_{\alpha\beta}\alpha'\beta'$ obtained using NMR data are represented best. The ferroelectricity in NaN$_2$ arises due to progressive ordering of the permanent electric dipoles associated with the NO$_2$ groups. Therefore, it is worthwhile to calculate the $M$-tensor components by obtaining changes in the electric field gradients produced at the 'Na' sites due to flipping motions of these dipoles. The electric field at a point $r$ due to a dipole of moment $p$ situated at origin is given by [35,36]

$$E(r) = \frac{1}{4\pi\epsilon_0} \left[ \frac{3(r \cdot p)}{r^5} - \frac{r - p}{r^3} \right] \quad (3)$$

where $\epsilon_0$ is the permittivity. The components $V_{\alpha\beta}$, i.e., $\partial^2V/\partial x_\alpha \partial x_\beta$ of the electric field gradient tensor, are obtained from this. Values of $V_{\alpha\beta}$ corresponding to two possible orientation of $p$ in which $p$ may jump, yield quantitatively, the fluctuation in $V_{\alpha\beta}$ and in turn the value of $M_{\alpha\beta}\alpha'\beta'$.

We have considered different possible flipping motions of NO$_2$. Since the polarization has a spiral orientation as one moves from one domain to the other.
[9], more attention was paid to flips about the axis \(a\) (i.e. \(y\)) or axes close to \(a\)-axis as shown by unit vector in Figure 3. It was found that a motion of \(NO_2\) where the dipole moment \(p\) flips by angle \(\theta \approx 85^\circ\) and \(\phi \approx 25^\circ\) yields value of M-tensor ratios close to the experimental values obtained from NMR data. For easy comparison the ratios \(M_{\alpha\beta\alpha'}\beta' / M_{zzz}\), where \(\alpha, \beta, \alpha', \beta'\) are \(x, y, z\) are given in Table I, along-with the experimental values. It is seen that the calculated values of all the ratios more or less match with the experimental values except \(M_{xxx}/M_{zzz}\). It indicates that larger changes occur along the \(x\)-direction. Inclusion of various shifting motions of Na ion in the model did not improve the match. Since the lattice dimensions have the relation \(a < b\) and \(b < c\) and in our coordinate system \(x, y, z\) axes are parallel to \(c, a, b\) respectively, it is more likely that the \(NO_2\) groups, while flipping about the \(a\)-axis, have less space to move and as a result get distorted while flipping through the angle \(\theta \approx 85^\circ\) and \(\phi \approx 25^\circ\). It is not possible in this model to take into account such distortion as these would change the values of \(|p|\) and this factor would get cancelled out while taking the ratios, also in this model, we have not considered the higher electric moments. Therefore, calculations based on point charge models were performed.

In the calculations of \(M\)-tensor components using point charge model, the \(NO_2\) group was considered as an assembly of three point charges with charges equal to \(-0.562e\) and \(+0.124e\) on 'O' and 'N' ions respectively [10]. The choice of the values of these charges is consistent with the anti-shielding factor. The electric field gradients were calculated using the expression of potential due to a point charge \(q_1\), at a distance \(r\) which is given as

\[
V = \frac{1}{4\pi \epsilon_0} \frac{q_1}{r}
\]
Changes in the components of efg were calculated by invoking a model where the NO$_2$ groups undergo a flipping motion about an arbitrary axis, not necessarily the axes $x$, $y$, $z$ (i.e. $c$, $a$, $b$). It was found that best match in the calculated and experimental values of $M_{||}$ are obtained when NO$_2$ groups are considered to flip through 170° about an axis whose direction cosines are 0.99, 0.11, 0.06 and 'Na' ion shifts by a very small amount (0.005Å) along $b$ axis. These values are given in Table I. As the $M$-tensor components vary as $r^{-6}$, only the six nearest NO$_2$ groups, four in the $a$-$c$ plane around 'Na' and one above and one below 'Na' along $b$ axis were considered. Various other motions of NO$_2$ groups and 'Na' ions were also considered, but did not show better results.

DISCUSSION

The calculated values of $M$-tensor components show better match with the experimental values when it is assumed that the dipoles associated with NO$_2$
groups flip through angle $\theta \approx 85^\circ$ and $\phi \approx 25^\circ$ i.e. do not flip about $a$, $b$ or $c$ axes, but flip about an axis inclined with respect to these. Also best match is obtained, for the calculations using point charge model when it is considered that the NO$_2$ groups flip by $170^\circ$ about an axis away from $a$, $b$ or $c$ and whose direction cosines are 0.99, 0.11 and 0.06. As pointed out earlier, calculations based on point charge model would be more accurate. It is worth mentioning that the electric polarization has a spiraling orientation as one moves from one domain to the other [9] as shown in Figure 2 and therefore any motion in conformation to this would be energetically favourable. It means that the polarization due to NO$_2$ groups would flip in such a way that its tip falls on a spiral with a pitch towards the axis $a$. Also, together with the flip, the 'Na' ion shifts in the $z(b)$ direction by a very small amount. It can be inferred that in ferroelectric NaNO$_2$, the NO$_2$ groups are undergoing $170^\circ$ flips about an axis having direction cosines 0.99, 0.11, 0.06 i.e. inclined away from $a$, $b$ and $c$ axes. This is schematically depicted in Figure 3. A flip by $170^\circ$ about the axis having direction cosines as mentioned above would lead to probably two possible locations where the tip of the polarization of NO$_2$ group would land after the flip. One location would be ahead of the plane where the NO$_2$ group dwelled before the flip, whereas the other location would be behind this plane. Both these would be such that the tip of the overall average polarization lies on a spiral as one moves from one domain to the other. For calculation of the changes in the components of the efg only one location has been considered. The possibility of more than one landing site indicates the situation where the vector representing the dipole moment of a NO$_2$ group would have a spread around the crystal symmetry axes ($b$-axis). It is to be mentioned that indeed the existence of a spread in the direction of local $b$-axis has been observed by the NMR line shape analysis in NaNO$_2$ by Hughes and Pandey[9].

It is conjectured that the electric polarization in some other order-disorder ferroelectrics also might have a spiral orientation and groups having permanent dipole moment, that are responsible for ferroelectricity in similar to that presented here may be followed to study the local motions using NMR data in those materials.

CONCLUSION

The local motions in the ferroelectric NaNO$_2$ were studied in the light of NMR results. It was found that a dynamical model involving the flipping motion of NO$_2$ groups about an axis having direction cosines 0.99, 0.11, 0.06 with respect to crystal coordinate system $c$, $a$, $b$ and slight shift of 'Na' in the $b$ direction rep-
resents the NMR data best. Such a motion conforms to the fact that in NaNO₂ crystal the electric polarization has a spiraling orientation as one moves from one domain to the other and to the fact that the local symmetry axis b has a spread about that determined by X-ray studies. Local motions in other order-disorder ferroelectrics may be studied in the same way using NMR data.

**Acknowledgements**

The financial support received from University Grants Commission, Bhopal and Department of Science and Technology, New Delhi, in form of research project, respectively by MK and LP, is gratefully acknowledged. LP is grateful to Prof. D. G. Hughes for useful discussions.

**References**