Electric Field Effect on NQR in Ferroelectric Materials* 

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The electric field effect on NQR in ferroelectric materials, 93Nb in LiNbO3 and 14N in NaNO3 and SC(NH2)2, has been investigated at 77 K. In these crystals with single domain, only the line shift due to the external electric field was observed. In the case of NaNO3 powder and a crystal with multidomains, line broadening was observed in the external electric field. These phenomena can be explained with the fact that the direction of spontaneous polarization in a domain is related to the direction of the applied electric field. The rate of the NQR line-shift due to the electric field is remarkably smaller in mostly ionic crystals, such as LiNbO3 and NaNO3, than in a molecular crystal such as SC(NH2)2. This is due to the strong ionic bonding in ionic crystals. Also, the difference of the Stark shift between NaNO3 and SC(NH2)2 is discussed in terms of the local electric field and polarizability at the resonant nuclear site.

Introduction

An external electric field applied to a nucleus located at a non-inversion symmetry site causes a change of the electric field gradient (e.f.g.) around the nucleus, expressed by [1–4]

\[ e(\Delta q)_{jk} = R_{ijk} E_i, \]  

where \( R_{ijk} \) is the component of the third rank tensor between the change in the e.f.g. tensor \( e(\Delta q)_{jk} \) and the applied electric field \( E_i \). As a result, a frequency shift due to the electric field is produced. In our experiment, we have observed the Stark effect on NQR in ferroelectric materials; 14N in NaNO3 [5] and SC(NH2)2, [6] and 93Nb in LiNbO3.

In this study, the NQR line-shift and -broadening in the above ferroelectric materials by the external electric field are discussed in terms of the domain structure of the crystals. Differences in the NQR line shift are understood in terms of the bonding characteristics of the crystal and the local electric field and polarizability at the resonant nuclear site.

Experimental Results

The NQR line measurements under the external electric field were made at 77 K in order to obtain a good signal to noise ratio and stable temperature, and to reduce the discharge current across the sample due to the applied high voltage. The NQR spectrometer was of the FET-adopted Robinson type [7]. An electric field up to \( \pm 50 \text{kV/cm} \) was applied either parallel or antiparallel to the direction of the spontaneous polarization \( P_s \) of the ferroelectric material.

For the single domain NaNO3 crystal, the frequency shift of the \( v^+ \) and \( v^- \) lines of 14N(\( I = 1 \)) NQR due to the external electric field is shown in Figs. 1a and 1b, respectively and evaluated in Table 1. \( E_+ (E_-) \) is the applied electric field parallel(antiparallel) to the direction of \( P_s \) along the crystallographic b-axis [8]. Actually, the measurements with \( E_+ \) were made first, and those with \( E_- \)-followed. For the multidomain crystal of NaNO3, the frequency broadening of the \( v^+ \) and \( v^- \) lines due to the external electric field is shown in Fig. 2 and evaluated in Table 1. The line broadening of the \( v^- \) line in NaNO3 powder, is shown in Fig. 3 and evaluated in Table 1.

Two lines \( |\pm 9/2\rangle \leftrightarrow |\pm 7/2\rangle \) and \( |\pm 7/2\rangle \leftrightarrow |\pm 5/2\rangle \) out of the four allowed transitions of 93Nb(\( I = 9/2 \)) NQR in LiNbO3 single crystal were detected: \( v_3 = 2.874 \text{MHz} \) and \( v_4 = 3.929 \text{MHz} \) at 77 K. The frequency shift of these lines due to the external electric field for the single domain crystal is shown in Fig. 4 and evaluated in Table 1. \( E_+ (E_-) \) is the applied electric field parallel(antiparallel) to the crystallographic c-axis, which is known as the direction of \( P_s \) [9].

For the 14N(\( I = 1 \)) NQR in ferroelectric SC(NH2)2, we expected two sets of two lines \( (v_1^+, v_1^-; v_2^+, v_2^-) \) due...
Table 1. The rate of shift and broadening of NQR lines in the domain states of ferroelectric materials

<table>
<thead>
<tr>
<th>Specimen</th>
<th>NaNO₂</th>
<th>LiNbO₃</th>
<th>SC(NH₂)₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>domain state</td>
<td>single</td>
<td>multi</td>
<td>powder</td>
</tr>
<tr>
<td>phenomena</td>
<td>line shift</td>
<td>line broadening</td>
<td>line shift</td>
</tr>
<tr>
<td>shift and broadening rate (Hz · cm/kV)</td>
<td>( \frac{dv^+}{dE} )</td>
<td>( \frac{d\Delta v^+}{dE} )</td>
<td>( \frac{d\Delta v^-}{dE} )</td>
</tr>
<tr>
<td>( 6.8 \pm 0.8 )</td>
<td>( 18.0 \pm 1.6 )</td>
<td>( 9.4 \pm 2.0 )</td>
<td>( 15.0 \pm 1.5 )</td>
</tr>
<tr>
<td>( 9.8 \pm 0.8 )</td>
<td>( 12.0 \pm 1.6 )</td>
<td>( 11.0 \pm 1.6 )</td>
<td>( 12.0 \pm 1.2 )</td>
</tr>
<tr>
<td>( 6.3 \pm 0.8 )</td>
<td>( 11.0 \pm 1.6 )</td>
<td>( 15.0 \pm 1.6 )</td>
<td>( 25.0 \pm 2.5 )</td>
</tr>
<tr>
<td>( 5.7 \pm 0.8 )</td>
<td>( 15.0 \pm 1.6 )</td>
<td></td>
<td>( 24.0 \pm 2.4 )</td>
</tr>
</tbody>
</table>

Fig. 1. The electric field dependence of the line shift a) for \( v^+ \) and b) for \( v^- \) in NaNO₂ single-domain crystal [5].

Fig. 2. The electric field dependence of the line broadening in NaNO₂ multi-domain crystal; (\( \Delta v^+ : \bullet \), \( \Delta v^- : \ast \)) [5].

Fig. 3. The electric field dependence of the line broadening for \( v^- \) in NaNO₂ powder [5].
The frequency shift due to the external electric field was measured for 3 lines out of 4, for the single domain crystal. The results for two lines are shown in Fig. 5 and evaluated in Table 1. \(E_+ (E_-)\) is the applied electric field parallel(antiparallel) to the \(b\)-axis, which is parallel to the direction of \(P_s\) [10]. The rates of the Stark shift for the ferroelectric \(\text{SC(NH}_2)_2\) are of the order of \(10^2\) times those for the ferroelectric \(\text{NaNO}_2\) and \(\text{LiNbO}_3\).

**Discussion**

The differences of the rate between the two situations of \(E_+\) and \(E_-\) in Table 1 appear to be a kind of ferroelectric hysteresis. NQR measurements under \(E_-\) were made with the same specimen following the measurements under \(E_+\). In case of \(\text{NaNO}_2, \text{LiNbO}_3\), and \(\text{SC(NH}_2)_2\) crystals with the single domain, the \(P_s\) is fixed along one direction. The applied electric field \(E_+ (E_-)\) means that it is parallel (antiparallel) to the...
direction of $P_s$, as shown in Figure 6a. The up-shift (down-shift) in frequency was observed with $E_+(E_-)$, as shown in Figs. 1, 4 and 5, without any detectable broadening of the linewidth. The applied electric field parallel(antiparallel) to $P_s$ causes $P_s$ to be increased (reduced). Therefore, the up-shift(down-shift) in frequency can be explained in terms of enhancement(reduction) of $P_s$ due to the applied electric field. In case of NaN0$_2$ crystal with multidomains, the direction of $P_s$ is alternately reversed with a phase difference of 180° between domains. Thus the applied electric field is parallel to $P_s$ in one kind of domains and antiparallel to $P_s$ in the other, as shown in Figure 6b. As a result of the up- and down-shift of the NQR line caused by the electric field in the single domain crystal, the line broadening is observed in the multidomain crystal without a line shift, as shown in Figure 2. In case of the powder sample of NaN0$_2$, the direction of $P_s$ of individual particles is randomly oriented with respect to the applied electric field, as shown in Figure 6c. Thus the line broadening, as shown in Figure 3, was observed.

NaN0$_2$ is an ionic crystal with some molecular character in the array of the NaN0$_2$ molecule [5, 11], and LiNbO$_3$ is also an ionic crystal with considerable covalency in the Nb-O bond [12]. SC(NH$_2$)$_2$ crystal is one of the rare examples of a molecular crystal showing a ferroelectric phase transition [13]. The ionic crystal is formed with a strong ionic bonding, whereas the molecular crystal is bonded with a weak van der Waals force. Furthermore, the intermolecular distances in SC(NH$_2$)$_2$ crystal are known to be greater than those due to the normal van der Waals force [10]. For these reasons, we can argue that the rate of the Stark shift of the molecular crystal SC(NH$_2$)$_2$ is remarkably larger than that of ionic crystals such as LiNbO$_3$ and NaN0$_2$, as summarized in Table 1. The change of the $P_s$ due to the external electric field is closely related to the local electric field ($E_{loc}$) and polarizability($\alpha$) at the resonant nucleus under consideration. The local electric field in NaN0$_2$ at the $^{14}$N site is known to be $E_{loc} = 2.0 \times 10^{10}$ V/m [14] from $P_s = 117$ mC/m$^2$ and $\alpha = 2.7 \times 10^{-30}$ m$^3$ [8]. Meanwhile, the local electric field and polarizability for SC(NH$_2$)$_2$ at the $^{14}$N site are calculated to be $E_{loc} = 0.36 \times 10^{10}$ V/m and $\alpha = 17 \times 10^{-30}$ m$^3$, respectively, using the Ewald transformation [15]. The small local electric field and large polarizability in SC(NH$_2$)$_2$ crystal means that the applied electric field is more effective to displace the electric dipoles in SC(NH$_2$)$_2$ than in NaN0$_2$. Therefore, the rate of the NQR line shift due to the electric field is remarkably larger in SC(NH$_2$)$_2$ than that in NaN0$_2$. 

![Diagram](image)
Acknowledgement

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