Electric Field Effect on ^{14}N NQR in Ferroelectric Thiourea Single Crystals*, **

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The electric field effect on ^{14}N NQR in ferroelectric thiourea [SC(NH$_2$)$_2$] single crystals has been investigated at 77 K up to a field of 10 kV/cm. The measured Stark shifts are, in units of kHz · cm/kV, $d\nu_1^+/dE_+ = 0.87 \pm 0.10$, $d\nu_1^+/dE_- = 1.17 \pm 0.20$, $d\nu_2^+/dE_+ = 0.80 \pm 0.10$, and $d\nu_2^+/dE_- = 0.90 \pm 0.15$. These values are on the order of 10^2 times those found in other ferroelectric crystals such as sodium nitrite (NaNO$_2$). The remarkable difference between these two Stark shifts is discussed by taking into account the polarizability and the local electric field at the ^{14}N sites in these crystals.

Key words: Electric field effect, Stark shift, ^{14}N NQR, Ferroelectric thiourea, Thiourea single crystal.

I. Introduction

The crystal structure of thiourea [SC(NH$_2$)$_2$] and its chemical properties have been studied by many investigators [1–4] since its ferroelectricity was first discovered by Solomon [1]. Subsequently, analysis of the low temperature structure and dielectric measurements were carried out by Goldsmith and White [2]. The found five phase transitions by measuring the dielectric constant. Smith and Cotts studied the temperature dependence of ^{14}N NQR in the ferroelectric phase (below $T_c = 169$ K) [3].

As an external effect on NQR, the changes in the quadrupole coupling of nuclei in a crystal due to strain and temperature are well established [3, 5]. Likewise, the applied electric field produces observable changes in the electric field gradient (e.f.g.) at the resonant nuclear site [5–9]. When this site has no inversion symmetry of the lattice, the linear effect in the applied electric field may be described phenomenologically by the relation

$$e(\Delta q)_{ij} = R_{kij} E_k, \quad (1)$$

where R is a third rank tensor between the change in the field gradient tensor $e\Delta q$ and the applied electric field E [5]. Colot already reported the Stark effect of NQR in thiourea [6]. However, he studied this effect with only one resonance line in powder.

In the present work, in order to obtain a more detailed electric field effect, we have investigated the Stark effect of ^{14}N NQR in thiourea single crystals at 77 K in the ferroelectric phase. The Stark effect appears to be remarkably dependent upon the bonding properties such as the ionic or molecular bonding of the crystal. The Stark shifts in thiourea are compared with those previously reported for sodium nitrite [7–9].

II. Crystal Structure of SC(NH$_2$)$_2$

The thiourea crystal exists below its decomposition temperature of approximately 433 K [3]. In all of its five phases, the crystal structure is orthorhombic with four molecules per unit cell and exhibits C$_{2v}$ symmetry in phase I (<169 K) and D$_{2h}$ symmetry in phase V (>202 K). The structure of the thiourea crystal at room temperature is shown in Figure 1. The lattice constants are $a = 5.520$, $b = 7.665$, and $c = 8.537$ Å at room temperature [2, 10]. The atoms in a molecule form a planar array, and they are arranged as shown in Figure 2. The C–S bond lies on the mirror plane normal to the paper of Fig. 2, and the electric dipole moment of the thiourea molecule lies along the C–S bond.

The phase transition from ferroelectric to antiferroelectric is explained by the existence of two types of

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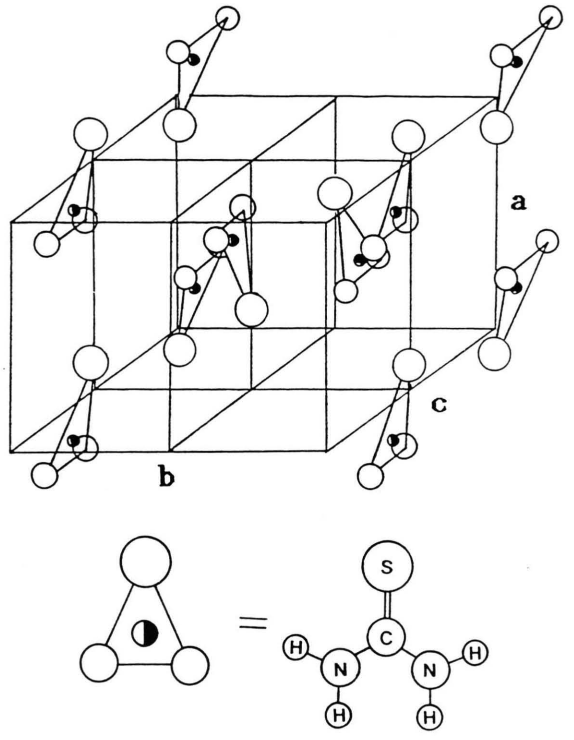

Fig. 1. The unit cell of a thiourea crystal at room temperature.

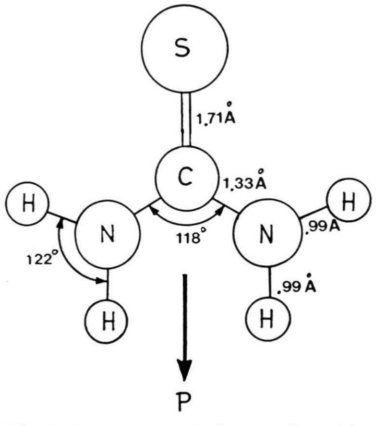

Fig. 2. Arrangement of atoms in a thiourea [$SC(NH_2)_2$] molecule. The bond distance and bond angles are indicated, and the arrow *p* represents the electric dipole moment.

projections of the molecular dipole onto the crystallographic ab-plane [11]. There are two pairs of molecular dipole moments in a unit cell in the ferroelectric phase; at 120 K, one pair (referred to as molecules 1) makes an angle of 70.4° with respect to the *b*-axis, and the other pair (molecules 2) makes an angle of 60.5°.

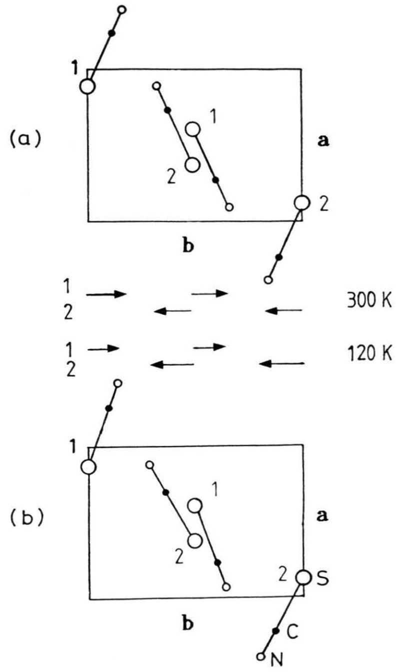

Fig. 3. The positions of the molecules 1 and 2 in the unit cell projected on the ab-plane (a) at room temperature (300 K) and (b) at low temperature (120 K). The dipole moment components along the *b*-axis are shown for both at the room and low temperature. The two pairs of dipole moments projected onto the *b*-axis do not cancel at low temperature, whereas they cancel completely at room temperature.

In the antiferroelectric phase at room temperature, the crystal structure is similar except that all the molecular dipoles make an identical angle of 63.4° relative to the *b*-axis; however, they are pairwise antiparallel to each other, so in this phase, all the dipole moments are cancelled. In all cases, the *c*-axis lies in the plane of the molecules and is perpendicular to their C–S bonds. The direction of the dipole moments of the thiourea molecules are changed according to the temperature, and this change determines their phases. These are shown in Figure 3. The ferroelectricity arises from the differently directed molecular dipoles with respect to the *b*-axis, so the spontaneous polarization is directed along the *b*-axis. The ferroelectric states are below 169 K and in between 176 and 180 K [2].

III. Theoretical Background

The nuclear quadrupole Hamiltonian for ^{14}N ($I=1$) is well known:

$$H_Q = [e^2 qQ/4I(2I-1)]\,[3I_z^2 - I^2 + \eta(I_+^2 + I_-^2)/2], \tag{2}$$

where $I_\pm = I_x \pm i\, I_y$, and $e\,Q$ is the electric quadrupole moment of the nucleus. The diagonal electric field gradient tensor is specified by five parameters: the largest component of the field gradient, V_{zz}; the asymmetry parameter η, $0 \leqq \eta \leqq 1$ as usual; and the three Euler angles specifying the directions of the principal axes. When the wavefunctions for the three magnetic quantum numbers ($m = 1$, 0, and -1) for the nuclear spin $I = 1$ of ^{14}N are given by Φ_1, Φ_0, and Φ_{-1}, respectively, then the diagonalized from of the Hamiltonian H_Q gives the following set of nondegenerate energy levels, E_i, and eigenfunctions Ψ_i:

$$\begin{aligned} E_{+1} &= e^2 q Q (1+\eta)/4, & \Psi_{+1} &= (\Phi_1 + \Phi_{-1})\, 2^{-1/2}, \\ E_{-1} &= e^2 q Q (1-\eta)/4, & \Psi_{-1} &= (\Phi_1 - \Phi_{-1})\, 2^{-1/2}, \\ E_0 &= -e^2 q Q/2, & \Psi_0 &= \Phi_0 . \end{aligned} \tag{3}$$

The transitions usually observed in experiments are those between the levels $E_{+1} \leftrightarrow E_0$ and $E_{-1} \leftrightarrow E_0$; they are referred to as ν^+ and ν^-, respectively, in terms of the frequency. For the case of thiourea in its ferroelectric phase, the electronic environments at the ^{14}N sites of the two pairs of molecules (molecules 1 and 2) are slightly different from each other as described in the crystal structure; consequently, two sets of two lines (ν_1^+ and ν_2^+, ν_1^- and ν_2^-) are expected.

IV. Experimental

A) Procedure

$SC(NH_2)_2$ single crystals were grown by evaporating a saturated methylalcohol solution at 30 °C for eight weeks. Obtained crystals had approximate dimensions of $0.9 \times 0.8 \times 0.6$ cm^3 and $0.4 \times 0.8 \times 0.5$ cm^3. In order to apply the electric field, electrodes were made by painting a silver paste on the broad faces cut normal to the *b*-axis, which is parallel to the spontaneous polarization (P_s) of this crystal. We employed a series connection of twenty 240-volt dry cells as a voltage source and connected electric fuses in series at every 1-kV step to prevent an accidental leakage current across the electrodes. The other experimental details are shown elsewhere [7]. The electric field was applied to the sample in two different situations, one parallel and the other antiparallel to the spontaneous polarization: E_+ ($E \uparrow\uparrow P_s$: parallel) and E_- ($E \uparrow\downarrow P_s$: antiparallel). The maximum intensity of the applied electric field was 10 kV/cm.

Table 1. Line widths (in kHz) of ^{14}N NQR in $SC(NH_2)_2$ and previously reported values in $NaNO_2$.

Specimen	Resonance line	Crystal	Powder	Ref.
$SC(NH_2)_2$	$\nu_{1.2}^+$	0.32 ± 0.05	0.90 ± 0.05	present
	$\nu_{1.2}^-$	0.22 ± 0.05	0.61 ± 0.05	work
$NaNO_2$	ν^+	0.66 ± 0.03	0.68 ± 0.03	[9], [13]
	ν^-	0.53 ± 0.03	0.56 ± 0.03	

The NQR signals were detected at 77 K under the electric field. This enabled us to obtain a good signal to noise ratio, to ensure the temperature stability of the sample, and to reduce the electric discharge current across the sample due to the applied high voltage. The NQR spectrometer employed here was a FET-adapted Robinson type [12].

B) Results

NQR signals were measured with $SC(NH_2)_2$ in single crystal and powder forms. The resonance line widths measured with the single crystal are observed to be nearly one third of those in powder. This ratio is in contrast to a previous report [3], in which the line widths in single crystal are about three times those in powder. However for $NaNO_2$ the line widths for the two forms are similar to each other [9, 13] (see Table 1).

In the ferroelectric phase of $SC(NH_2)_2$, there are two pairs of physically inequivalent molecules as shown in Figure 3. Since the electric field gradients at the two ^{14}N sites (molecules 1 and 2) are slightly different from each other, four resonance lines are observed. We have measured the behavior of these signals as a function of the external electric field at 77 K. The measured Stark shifts of the two ν^+ signals are: $d\nu_1^+/dE_+ = 0.87 \pm 0.18$, $d\nu_1^+/dE_- = 1.17 \pm 0.20$, $d\nu_2^+/dE_+ = 0.80 \pm 0.10$, and $d\nu_2^+/dE_- = 0.90 \pm 0.15$ kHz · cm/kV. For the ν^- signal, $d\nu_1^-/E_+$ is 0.84 ± 0.10 kHz · cm/kV. These Stark shifts in thiourea are on the order of 10^2 times those previously reported for $NaNO_2$ [8, 9] and listed in Table 2.

V. Discussion

Experimental evidence [5, 8, 9] revealed that the shift of NQR frequency is up (down) for E_+ (E_-) with respect to the spontaneous polarization. When an

Table 2. Stark shifts of ^{14}N NQR in $SC(NH_2)_2$ and reported values of $NaNO_2$.

Stark shift	Molecular sites	$SC(NH_2)_2$ (kHz · cm/kV)	$NaNO_2$ [9] (Hz · cm/kV)
$d\nu^+/dE_+$	1	0.87 ± 0.18	6.8 ± 3.0
	2	0.80 ± 0.10	
$d\nu^+/dE_-$	1	1.17 ± 0.20	9.8 ± 2.2
	2	0.90 ± 0.15	
$d\nu^-/dE_+$	1	0.84 ± 0.10	6.3 ± 2.0
	2		
$d\nu^-/dE_-$	1		5.7 ± 2.0
	2		

Table 3. Comparison of the crystal properties of $SC(NH_2)_2$ and $NaNO_2$.

Crystal property	$SC(NH_2)_2$	$NaNO_2$
$P_s (mC/m^2)$	30	117
$\alpha (m^3)$	17×10^{-30}	2.7×10^{-30}
E_{loc}	3.6×10^9	2.0×10^{-10}
bonding force	van der Waals	mostly ionic

electric field is applied to a crystal for NQR measurements, a polarization is induced; the electric field applied along the ferroelectric axis increases (reduces) the P_s of the crystal for $E \uparrow\uparrow P_s$ ($E \uparrow\downarrow P_s$). The experimental results of the present work are similar to other cases. Thus, the line shifts of ^{14}N NQR in $SC(NH_2)_2$ may be explained in terms of the change of P_s due to the applied electric field.

The four molecules in the unit cell are known to be two inequivalent pairs, with different inclinations to the *b*-axis, which is parallel to P_s. From the geometries of the two pairs of molecules shown in Fig. 3, the spontaneous polarization is given by [11]

$$P_s = 2(p \sin\theta_2 - p \sin\theta_1)/V = \frac{4p}{V} \cdot \cos\frac{\theta_1+\theta_2}{2} \cdot \sin\frac{\theta_2-\theta_1}{2}, \tag{4}$$

where p is the dipole moment of the molecule, V is the volume of the unit cell, and θ_1 (θ_2) is the angle between the dipole moment of molecules 1 (2) and the *b*-axis. If θ_1 and θ_2 are expressed as $\theta_0 + \theta$ and $\theta_0 - \theta$, respectively, then θ_0 is assumed to be independent of temperature in the ferroelectric region ($\theta_0 = 65.5°$ at 120 K) [10]. Thus

$$P_s = 4p \cos\theta_0 \cdot \sin\theta / V. \tag{5}$$

For small θ, P_s is proportional to θ. Goldsmith and White concluded that the change of polarization was caused by the action of the field on the resultant of the dipole moments of the molecules in the [010] direction [2]. This means that the electric field should cause the molecules to turn and change their tilts, θ_1 and θ_2, with respect to the [010] direction. The change of the tilt by the external electric field is closely related to the polarizability (α) and the local electric field (E_{loc}) around the resonant nucleus under consideration. For $SC(NH_2)_2$, Elcombe and Taylor calculated the average values of E_{loc} and α at the ^{14}N atomic sites, using the Ewald transformation [10]; $E_{loc} = 3.6 \times 10^9$ V/m, and $\alpha = 17 \times 10^{-30}\,m^3$ in SI units. Meanwhile, the value of E_{loc} around the ^{14}N site in $NaNO_2$ is known to be 2.0×10^{10} V/m [7], from $P_s = 117\,mC/m^2$ and $\alpha = 2.7 \times 10^{-30}\,m^3$ [14]. These values of $SC(NH_2)_2$ are summarized in Table 3 together with those for $NaNO_2$. The polarizability of thiourea is 6 times larger than that of $NaNO_2$, while the value of E_{loc} at the ^{14}N site in $SC(NH_2)_2$ is 6 times smaller than that around the NO_2^- radical of $NaNO_2$. This means that the applied electric field can be more effective in turning the molecular dipole in thiourea than in $NaNO_2$.

Therefore, the larger Stark shift of ^{14}N NQR in thiourea than that in sodium nitrite may be qualitatively interpreted by means of the rather smaller local electric field and the relatively larger polarizability. Sodium nitrite is an ionic crystal with some molecular character in the array of the $NaNO_2$ molecule [9, 15], and thiourea is a molecular one [3]. The ionic crystal is formed with a strong ionic bonding, whereas the molecular crystal is due to a weak van der Waals bonding. Furthermore, the intermolecular distances in thiourea crystal were known to be greater than those due to the normal van der Waals interaction [2]. For these reasons, we can argue that the Stark shift of NQR in a molecular crystal is greater than that in an ionic one. This is supported by the other reported experimental evidence listed in Table 4 [16, 17].

Meanwhile, Colot briefly mentioned a Stark shift on the order of 10 Hz · cm/kV in $SC(NH_2)_2$ powder as a preliminary measurement [6]. This value is quite different from ours. As he used a powder sample, he might have obtained the line broadening rather than the line shift due to the random orientation of the applied electric field with respect to the P_s of individual particles. Since we measured the Stark shift of several lines for the thiourea single crystal, we believe our results are more reliable.

Table 4. Comparison of the Stark shifts between molecular and ionic crystals.

	Compound	Resonance nucleus	Stark shift (kHz · cm/kV)	Ref.
molecular crystal	$Co_{10}Re_2$	^{185}Re	1.7	[16], [17]
	p-$C_6H_4$$^{127}I$	^{127}I	0.93	
	p-$C_6H_4$$^{81}Br$	^{81}Br	0.61	
	$HgCl_2$	^{35}Cl	0.12	
	$SnCl_4$	^{35}Cl	0.13	
	$SC(NH_2)_2$	^{14}N	0.84*	present work
mostly ionic crystal	$NaClO_3$	^{35}Cl	0.018	[5]
	$NaNO_2$	^{14}N	0.0068	[8], [9]

* for the ν^- line.

VI. Conclusion

Since the e.f.g. at the ^{14}N nucleus is closely related to the local electric field (E_{loc}) and the polarizability (α) at the nitrogen atom in the crystal, the shifts of the ^{14}N NQR lines may be interpreted by means of the local electric field and the polarizability of the crystal. The measured Stark shifts in thiourea are on the order of 10^2 times those previously reported for $NaNO_2$. The difference of the Stark shifts in these two crystals may be qualitatively understood by comparing the bonding properties of the crystals. The larger Stark shifts of ^{14}N in $SC(NH_2)_2$ can be interpreted by means of the relatively smaller local electric field and the larger polarizability at the ^{14}N atom. One can conclude that the changes in the e.f.g. at a resonant nucleus due to the external electric field are, in general, more pronounced in a molecular crystal than in an ionic one.

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