

A Note on the ¹⁴N Electric Field Gradient Tensors in Incommensurate [N(CH₃)₄]₂ZnCl₄

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The ¹⁴N electric field gradient tensors of [N(CH₃)₄]₂ZnCl₄ have been re-determined in the paraelectric phase at 26 °C and in the incommensurate phase at 16 °C. The results in the incommensurate phase show the “non-local” nature of the ¹⁴N EFG tensor interaction.

Tetramethylammonium tetrachlorozincate [N(CH₃)₄]₂ZnCl₄ (TMATC-Zn) belongs to the group of A₂BX₄ crystals. It first transforms with decreasing temperature from the normal (P) to the incommensurate (I) phase and then exhibits at lower temperatures a sequence of commensurate (C) phases. In a recent paper [1] we reported on the ¹⁴N EFG tensors of TMATC-Zn in the paraelectric phase at 26 °C

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Table 1. ¹⁴N EFG tensors in the crystal fixed frame in paraelectric TMATC-Zn expressed in frequency units (kHz), i.e. multiplied by 3e Q/2h.

$T_0(1,2) = \begin{vmatrix} 19.5 & 0 & 0 \\ 0 & 42.5 \pm 4 & \\ 0 & \pm 4 & -62 \end{vmatrix}; (e^2qQ/h)_{1,2} = 41.4 \text{ kHz}$	$\eta_{1,2} = 0.373$
$T_0(3,4) = \begin{vmatrix} -78 & 0 & 0 \\ 0 & 89 \pm 48.5 & \\ 0 & \pm 48.5 & -11 \end{vmatrix}; (e^2qQ/h)_{3,4} = 72.4 \text{ kHz}$	$\eta_{3,4} = 0.436$

Table 2. ¹⁴N EFG tensors in kHz in the I phase of TMATC-Zn expressed in the crystal fixed a, b, c frame:

$T(x) = T_0 + T_{1''} \cos[\Phi(x) - \Phi_1] + \frac{1}{2} T_{2'} + \frac{1}{2} T_{2''} \cos 2[\Phi(x) - \Phi_2]$											
	$T_{1''}$			$T_{2'}$			$T_{2''}$			Φ_1	$\Phi_2 = 0$
$i = 1, 2$	0	6	12	0	0	0	-5	0	0	0	45°
	6	0	0	0	2	±0.5	0	9	4	45°	0
	12	0	0	0	±0.5	-0.5	0	4	-4	45°	0
$i = 3, 4$	0	5.5	7	-1	0	0	2	0	0	0	45°
	5.5	0	0	0	1.5	±5	0	2.5	5	45°	0
	7	0	0	0	±5	1	0	5	-3	45°	0

and in the I phase at 16 °C. In that paper the b and c rotations did not correspond to precise rotations about the b and c crystallographic axes, but instead those two axes were tilted for a small angle ($\theta \approx 4^\circ$) with respect to the rotation axes. This lead to a slight misinterpretation of the ¹⁴N EFG tensors which we would like to correct here.

In the paraphase, which has the space group Pmcn, there are four physically and two chemically nonequivalent ¹⁴N sites in the unit cell. The ¹⁴N nuclei lie on the b–c mirror plane. The two groups of chemically nonequivalent ¹⁴N nuclei can be divided into two sub-groups of physically nonequivalent ¹⁴N nuclei. These two subgroups are related by the glide symmetry which requires the b and c principal axes of the two corresponding physically nonequivalent ¹⁴N EFG tensors to be rotated symmetrically about the a principal axis, where a lies normal to the b–c mirror plane.

One thus expects in the paraphase four different ¹⁴N EFG tensors, where each of the two physically nonequivalent EFG tensors is of the form

$$T_0^\pm = \begin{vmatrix} T_0^{aa} & 0 & 0 \\ 0 & T_0^{bb} & \pm T_0^{bc} \\ 0 & \pm T_0^{bc} & T_0^{cc} \end{vmatrix}, \quad T > T_1. \quad (1)$$

The symmetry of the particular physically non-equivalent tensor in the I phase is described in [1], where it is shown that each tensor element $T^{(\mu)}$ can be expanded in powers of the nuclear displacements from their high temperature equilibrium sites as:

$$T^{(\mu)}(x) = T_0^{(\mu)} + T_1^{(\mu)} \cos[\Phi(x) - \Phi_1^{(\mu)}] + \frac{1}{2} T_2^{(\mu)} + \frac{1}{2} T_2^{(\mu)} \cos 2[\Phi(x) - \Phi_2^{(\mu)}] + \dots \quad (2)$$

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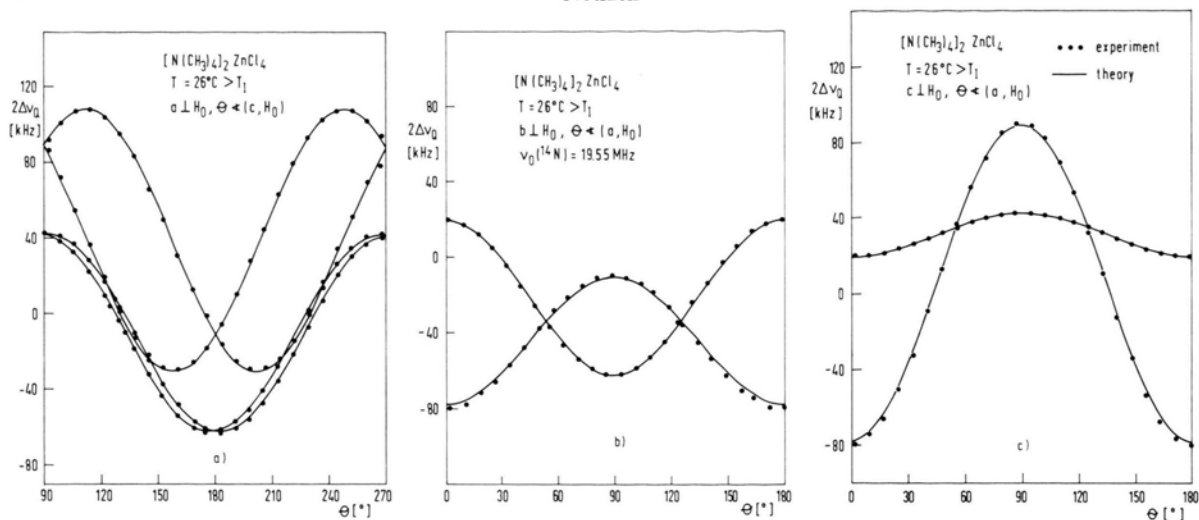


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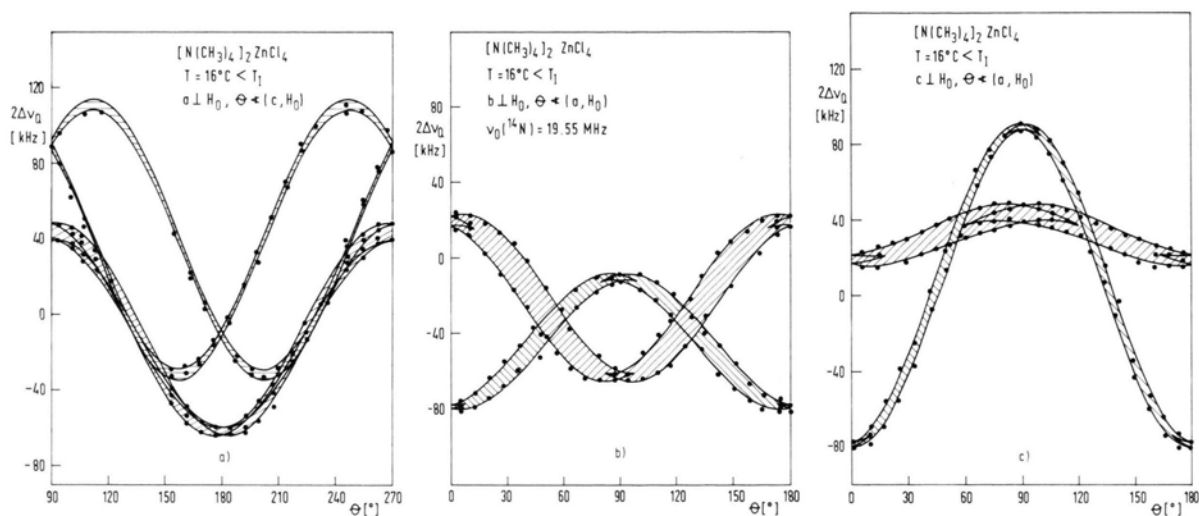
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Figs. 1 a, b, c. Angular dependence of the quadrupole splitting of the ^{14}N spectra in TMATC-Zn at $26^\circ\text{C} > T_1$. The full line is the theoretical fit.



Figs. 2a, b, c. Angular dependence of the incommensurate frequency distribution singularities in the ^{14}N spectra of TMATC-Zn in the I phase at $16^\circ\text{C} < T_1$. The full line is the theoretical fit for the "non-local" model. The hatched area indicates the quasi-continuous distribution of the ^{14}N transition frequencies.

The angular dependence of the ^{14}N quadrupole splitting $2\Delta v_Q$ for $T = 26^\circ\text{C} > T_1$ is shown in Figs. 1a, b, c for rotation around the a , b and c crystal axes. The results show the existence of four physically (and two groups of chemically) nonequivalent ^{14}N sites (Table 1). The experimental error is about ± 2 kHz.

In the I phase at $T = 16^\circ\text{C} < T_1$, $T_0(i)$, $i = 1-4$ is not changed but $T_{1''}(i)$, $T_{2''}(i)$ and $T_{2'}(i)$ are non-

zero and can be determined from the angular variation [1] (Figs. 2a-c) of the incommensurate frequency distribution singularities. The results are collected in Table 2. The discussion of the results within the "non-local" model [2] is, however, correctly described in [1].

[1] J. Dolinšek and R. Blinc, Z. Naturforsch. **41a**, 265 (1986).

[2] R. Blinc, J. Seliger, and S. Žumer, J. Phys. C **18**, 2313 (1985).