A Note on the ^{14}N Electric Field Gradient Tensors in Incommensurate $[N(CH_3)_4]_2ZnCl_4$

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The ^{14}N electric field gradient tensors of $[N(CH_3)_4]_2ZnCl_4$ 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 ^{14}N EFG tensor interaction.

Tetramethylammonium tetrachlorozincate $[N(CH_3)_4]_2ZnCl_4$ (TMATC-Zn) belongs to the group of A_2BX_4 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 ^{14}N EFG tensors of TMATC-Zn in the paraelectric phase at 26 °C 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 ($\theta \approx 4°$) with respect to the rotation axes. This lead to a slight misinterpretation of the ^{14}N EFG tensors which we would like to correct here.

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In the paraphase, which has the space group Pmcn, there are four physically and two chemically nonequivalent ^{14}N sites in the unit cell. The ^{14}N nuclei lie on the $b-c$ mirror plane. The two groups of chemically nonequivalent ^{14}N nuclei can be divided into two sub-groups of physically nonequivalent ^{14}N nuclei. These two subgroups are related by the glide symmetry which requires the b and c principal axes of the two corresponding physically nonequivalent ^{14}N 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 ^{14}N EFG tensors, where each of the two physically nonequivalent EFG tensors is of the form

$$\mathbf{T}_0^{\pm} = \begin{vmatrix} T_0^{aa} & 0 & 0 \\ 0 & T_0^{bb} & \pm T_0^{bc} \\ 0 & \pm T_0^{bc} & T_0^{cc} \end{vmatrix}, \quad T > T_1. \qquad (1)$$

The symmetry of the particular physically nonequivalent 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:

$$T^{(\mu)}(x) = T_0^{(\mu)} + T_{1''}^{(\mu)} \cos[\Phi(x) - \Phi_1^{(\mu)}] + \tfrac{1}{2} T_{2'}^{(\mu)} + \tfrac{1}{2} T_{2''}^{(\mu)} \cos 2[\Phi(x) - \Phi_2^{(\mu)}] + \dots \qquad (2)$$

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

$$\mathbf{T}_0(1,2) = \begin{vmatrix} 19.5 & 0 & 0 \\ 0 & 42.5 & \pm 4 \\ 0 & \pm 4 & -62 \end{vmatrix}; \quad (e^2qQ/h)_{1,2} = 41.4\ \text{kHz}, \quad \eta_{1,2} = 0.373$$

$$\mathbf{T}_0(3,4) = \begin{vmatrix} -78 & 0 & 0 \\ 0 & 89 & \pm 48.5 \\ 0 & \pm 48.5 & -11 \end{vmatrix}; \quad (e^2qQ/h)_{3,4} = 72.4\ \text{kHz}, \quad \eta_{3,4} = 0.436$$

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

$$\mathbf{T}(x) = \mathbf{T}_0 + \mathbf{T}_{1''} \cos[\Phi(x) - \mathbf{\Phi}_1] + \tfrac{1}{2}\mathbf{T}_{2'} + \tfrac{1}{2}\mathbf{T}_{2''} \cos 2[\Phi(x) - \mathbf{\Phi}_2]$$

	$\mathbf{T}_{1''}$			$\mathbf{T}_{2'}$			$\mathbf{T}_{2''}$			$\mathbf{\Phi}_1$			$\mathbf{\Phi}_2 = 0$
$i = 1,2$	0	6	12	0	0	0	−5	0	0	0	45°	45°	
	6	0	0	0	2	±0.5	0	9	4	45°	0	0	
	12	0	0	0	±0.5	−0.5	0	4	−4	45°	0	0	
$i = 3,4$	0	5.5	7	−1	0	0	2	0	0	0	45°	45°	
	5.5	0	0	0	1.5	±5	0	2.5	5	45°	0	0	
	7	0	0	0	±5	1	0	5	−3	45°	0	0	

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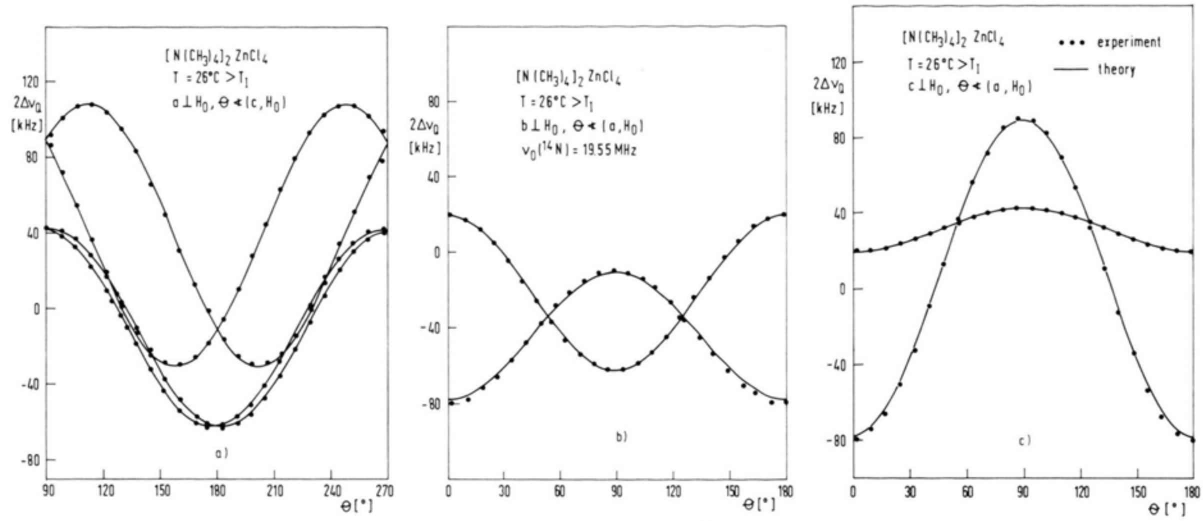
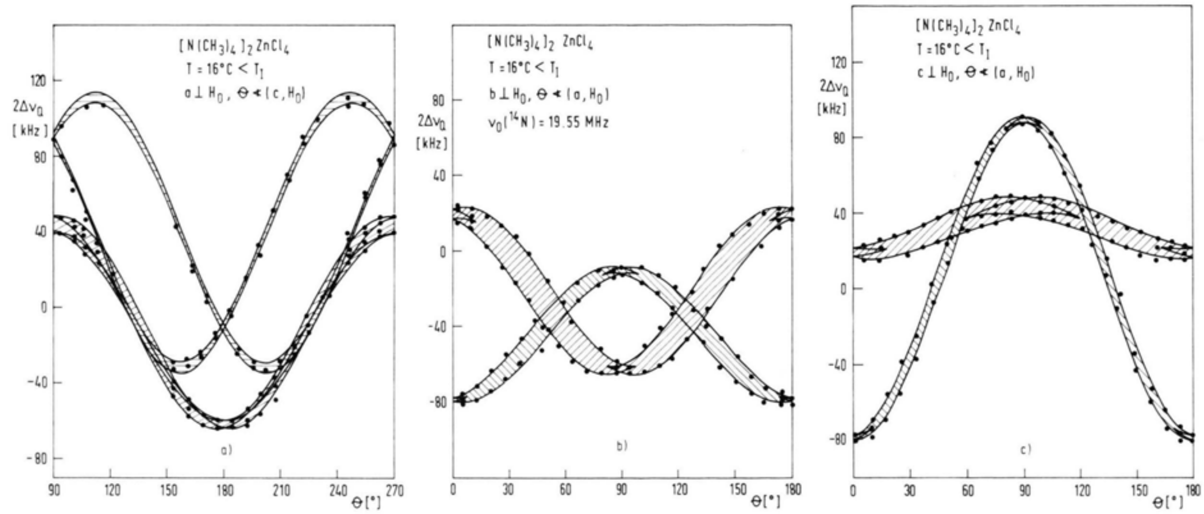


Figs. 1a, b, c. Angular dependence of the quadrupole splitting of the ^{14}N spectra in TMATC-Zn at $26\,°C > T_I$. The full line is the theoretical fit.



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 $16\,°C < T_I$. 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 $2\Delta\nu_Q$ for $T = 26\,°C > T_I$ 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 $\pm\,2$ kHz.

In the I phase at $T = 16\,°C < T_I$, $\mathbf{T}_0(i)$, $i = 1-4$ is not changed but $\mathbf{T}_{1''}(i)$, $\mathbf{T}_{2''}(i)$ and $\mathbf{T}_{2'}(i)$ are nonzero 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. **41 a,** 265 (1986).

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