A Note on the $^{14}$N Electric Field Gradient Tensors in Incommensurate [N(CH$_3$)$_4$]$_2$ZnCl$_4$

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The $^{14}$N electric field gradient tensors of [N(CH$_3$)$_4$]$_2$ZnCl$_4$ 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$_3$)$_4$]$_2$ZnCl$_4$ (TMATC-Zn) belongs to the group of A$_2$B$_x$ 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 (θ ≈ 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.

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

\[
T_0 = \begin{bmatrix} T_{0}^{ab} & 0 & 0 \\ 0 & T_{0}^{bc} & \pm T_{0}^{ce} \\ 0 & \pm T_{0}^{be} & T_{0}^{ce} \end{bmatrix}, \quad T > T_1. \tag{1}
\]

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

\[
T_{ij}^{(a)}(x) = T_{ij}^{(a)} + \frac{1}{2} T_{ij}^{(a)} \cos \Phi(x) - \Phi_{ij}^{(a)} + \frac{1}{2} T_{ij}^{(a)} \cos 2\Phi(x) - \Phi_{ij}^{(a)},
\]

where $\Phi_{ij}^{(a)} = \Phi_{ij}^{(a)}$, $T_{ij}^{(a)}$, $\Phi_{ij}^{(a)}$, $T_{ij}^{(a)}$, and $\Phi_{ij}^{(a)}$ are the tensor elements and rotation angles, respectively.

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

\[
\begin{array}{cccc}
T_{0}(1,2) & 0 & 42.5 \text{±} & 4 \\
0 & 0 & 0 \\
42.5 \text{±} & 4 & 0 \\
0 & 0 & 0 \\
\end{array}
\]

\[
\begin{array}{cccc}
0 & 0 & 0 \\
0 & 0 & 0 \\
42.5 \text{±} & 4 & 0 \\
0 & 0 & 0 \\
\end{array}
\]

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

\[
T(x) = T_0 + T_1 \cos[\Phi(x) - \Phi_1] + \frac{1}{2} T_2 + \frac{1}{2} T_3 \cos 2[\Phi(x) - \Phi_2]
\]

\[
\begin{array}{cccccccc}
T_1 & T_2 & T_3 & \Phi_1 & \Phi_2 \\
0 & 6 & 12 & 0 & 0 & 0 & 0 & 45^\circ & 45^\circ \\
6 & 0 & 0 & 0 & 0 & 2 & \pm & 0.5 & 45^\circ & 0 \\
0 & 6 & 0 & 0 & 0 & 0 & 0 & -0.5 & 45^\circ & 0 \\
12 & 0 & 0 & 0 & 0 & 0 & 0 & 4 & 0 & 0 \\
5.5 & 0 & 0 & 0 & 0 & 1.5 & \pm & 0.5 & 0 & 0 \\
0 & 5 & 0 & 0 & 0 & 0 & 0 & 0 & 45^\circ & 0 \\
7 & 0 & 0 & 0 & 0 & 0 & 0 & 5 & 3 & 45^\circ & 0 \\
\end{array}
\]

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The angular dependence of the $^{14}$N quadrupole splitting $2\Delta v_0$ for $T = 26^\circ C > T_1$ 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 $\pm 2$ kHz.

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