^{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 have been determined in the paraelectric phase at $T = 26\,°C$ and in the incommensurate phase at $T = 16\,°C$. The results in the incommensurate phase are typical for the "non-local" case and show the presence of two out of phase components of the modulation wave. The phase shift between the linear and the quadratic terms in the expansion of the frequency in powers of the order parameter is as large as $45°$.

I. Introduction

Tetramethylammonium tetrachlorozincate $[N(CH_3)_4]_2 ZnCl_4$ (TMATC-Zn) belongs to the group of A_2BX_4 crystals which first transform from the normal (P) to the incommensurate (I) phase and then exhibit at lower temperatures a series of commensurate (C) phases. In TMATC-Zn the transitions [1, 2, 3, 4] at $T_I = 23\,°C$, $T_{c1} = 7\,°C$, $T_{c2} = 3.5\,°C$, $T_{c3} = -96\,°C$ and $T_{c4} = -117\,°C$ are connected with changes in the magnitude of the cell dimension along the direction of the pseudo-hexagonal axis: c_0, $\sim 5c_0$, $5c_0$, $3c_0$, c_0 and $3c_0$. The corresponding space groups are [2] D_{2h}^{16}-Pmcn ($z = 4$), incommensurate, C_{2v}^9-P2$_1$cn ($z = 20$), C_{2h}^9-P112$_{1/n}$, ($z = 12$), C_{2h}^5-P12$_{1/c_1}$ ($z = 4$) and D_2^4-P2$_1$2$_1$2$_1$ ($z = 12$). It has been proposed [4] that the phase transition sequence in TMATC-Zn may form part of a devil's staircase.

The orthorhombic unit cell dimensions in the room temperature D_{2h}^{16} paraelectric phase are $a = 8.998$ Å, $b = 15.541$ Å and $c = 12.276$ Å. The ^{14}N nuclei lie on the b-c mirror plane. There are four physically and two chemically non-equivalent ^{14}N sites. In the I phase the modulation wave vector equals $\boldsymbol{q}_I = (1 - \delta) \cdot \boldsymbol{c}^* \cdot (2/5)$. The nuclear displacements are perpendicular to the b-c mirror plane and the translational periodicity of the crystal is lost. All ^{14}N sites in the crystal are non-equivalent

resulting in a distribution of the ^{14}N electric field gradient (EFG) tensors.

^{13}C NMR [5] has shown a rapid hindered rotation of the distorted N-$(CH_3)_4$ tetrahedra around at least three orthogonal axes as well as the rotation of the methyl groups around their C_3 axis. As a result of this motion the ^{14}N EFG tensors should be motionally averaged to a small but finite value which depends on the distortion of the N-$(CH_3)_4$ groups.

The changes in the EFG tensor induced by the incommensurable modulation wave at the position of the α-th ^{14}N nucleus can be [6], up to second order terms, expressed as

$$\mathbf{T} = \mathbf{T}_0 + \mathbf{T}_1 + \mathbf{T}_2 + \ldots , \qquad (1)$$

where

$$\mathbf{T}_1 = \sum_j \nabla_j \mathbf{T}_0 \, \boldsymbol{u}_j \, \alpha \, (\varDelta T)^\beta \qquad (2\,a)$$

and

$$\mathbf{T}_2 = \sum_{j, j'} \boldsymbol{u}_{j'} \, \nabla_{j'} (\nabla_j \mathbf{T}_0) \, \boldsymbol{u}_j \, \alpha \, (\varDelta T)^{2\beta} \qquad (2\,b)$$

with $\mathbf{T}_0$ standing for the paraelectric EFG tensor. In view of symmetry considerations [7, 8, 9, 10] one expects that

$$\mathbf{T}_0 = \begin{vmatrix} T_0^{aa} & 0 & 0 \\ 0 & T_0^{bb} & T_0^{bc} \\ 0 & T_0^{bc} & T_0^{cc} \end{vmatrix} ; \qquad (3\,a)$$

$$\mathbf{T}_1 = \begin{vmatrix} 0 & T_1^{ab} & T_1^{ac} \\ T_1^{ab} & 0 & 0 \\ T_1^{ac} & 0 & 0 \end{vmatrix} ; \qquad (3\,b)$$

$$\mathbf{T}_2 = \begin{vmatrix} T_2^{aa} & 0 & 0 \\ 0 & T_2^{bb} & T_2^{bc} \\ 0 & T_2^{bc} & T_2^{cc} \end{vmatrix} . \qquad (3\,c)$$

a)

b)

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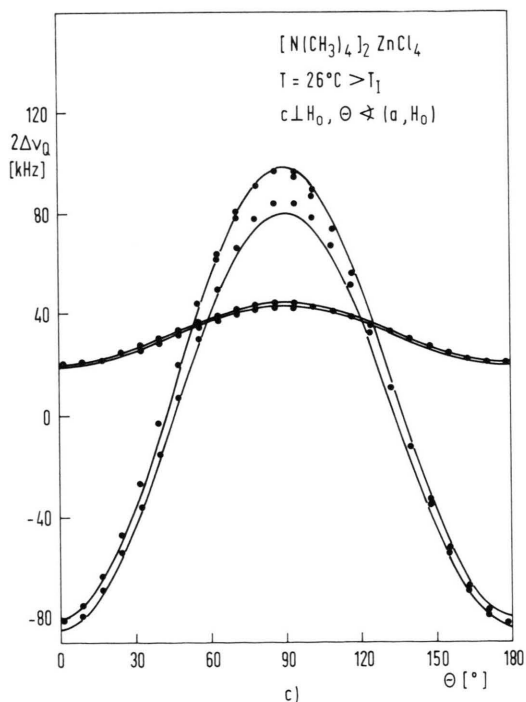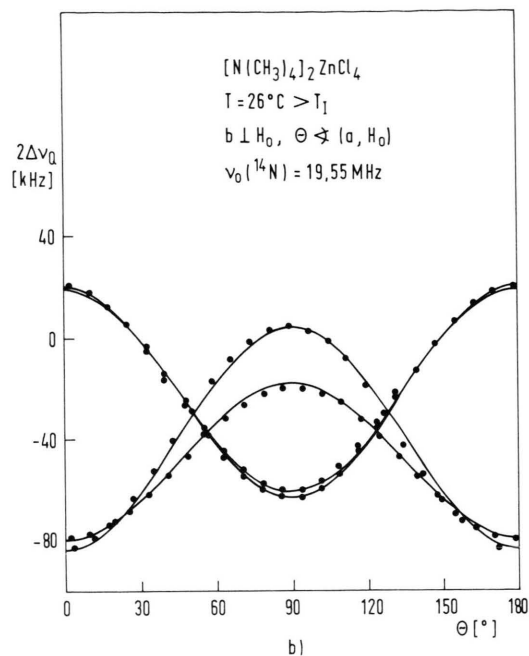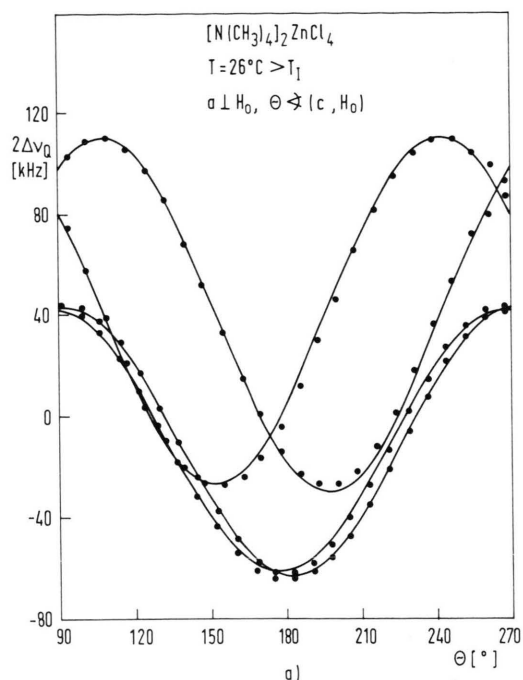
Fig. 1. Angular dependence of the quadrupole splitting of the ^{14}N spectra in TMATC-Zn at $T = 26\,°C > T_I$. The full line is the theoretical fit.

The real displacement $\boldsymbol{u}_j$ of the α-th nucleus in the l-th unit cell is given by a admixture of a symmetric and an antisymmetric component of the modulation wave

$$\boldsymbol{u}_j = \boldsymbol{u}_{0\alpha}^c \cos \Phi\,(x_j) + \boldsymbol{u}_{0\alpha}^s \sin \Phi\,(x_j), \qquad (4\,\mathrm{a})$$

so that

$$u_{jk} = u_{0\alpha k} \cos\,[\Phi\,(x_j) + \varphi_{0\alpha k}], \quad k = x, y, z, \qquad (4\,\mathrm{b})$$

where $\varphi_{0\alpha k}$ is different for different nuclei in the unit cell and $\Phi\,(x) = \boldsymbol{q}_c\,\boldsymbol{x}_\alpha + \varphi\,(x)$. Here $\boldsymbol{q}_c$ is the C wave vector, $\varphi\,(x)$ a solution of the sine-Gordon equation, and $\boldsymbol{x}_\alpha(l) = \boldsymbol{x}_{0\alpha} + l\,\boldsymbol{c}$, $l = 0, 1, 2, 3, \dots$ with $\boldsymbol{x}_{0\alpha}$ denoting the position of the α-th nucleus in the l-th unit cell.

The expansion of the EFG tensor components in powers of the nuclear displacements now becomes [6]

$$T^{(\mu)}(x) = T_0^{(\mu)} + T_1^{(\mu)} \cos\,[\Phi\,(x) - \Phi_1^{(\mu)}] + \tfrac{1}{2}\,T_2^{(\mu)}$$
$$+ \tfrac{1}{2}\,T_2^{(\mu)} \cos 2\,[\Phi\,(x) - \Phi_2^{(\mu)}] + \dots. \qquad (5)$$

If the contributions to the EFG tensor are of a local nature [6] and if $\boldsymbol{u}_0^c$ and $\boldsymbol{u}_0^s$ in (4a) are parallel one finds that $\Phi_1^{(\mu)} - \Phi_2^{(\mu)} = 0$ and that $T_2^{(\mu)} = T_2^{(\mu)}$. It
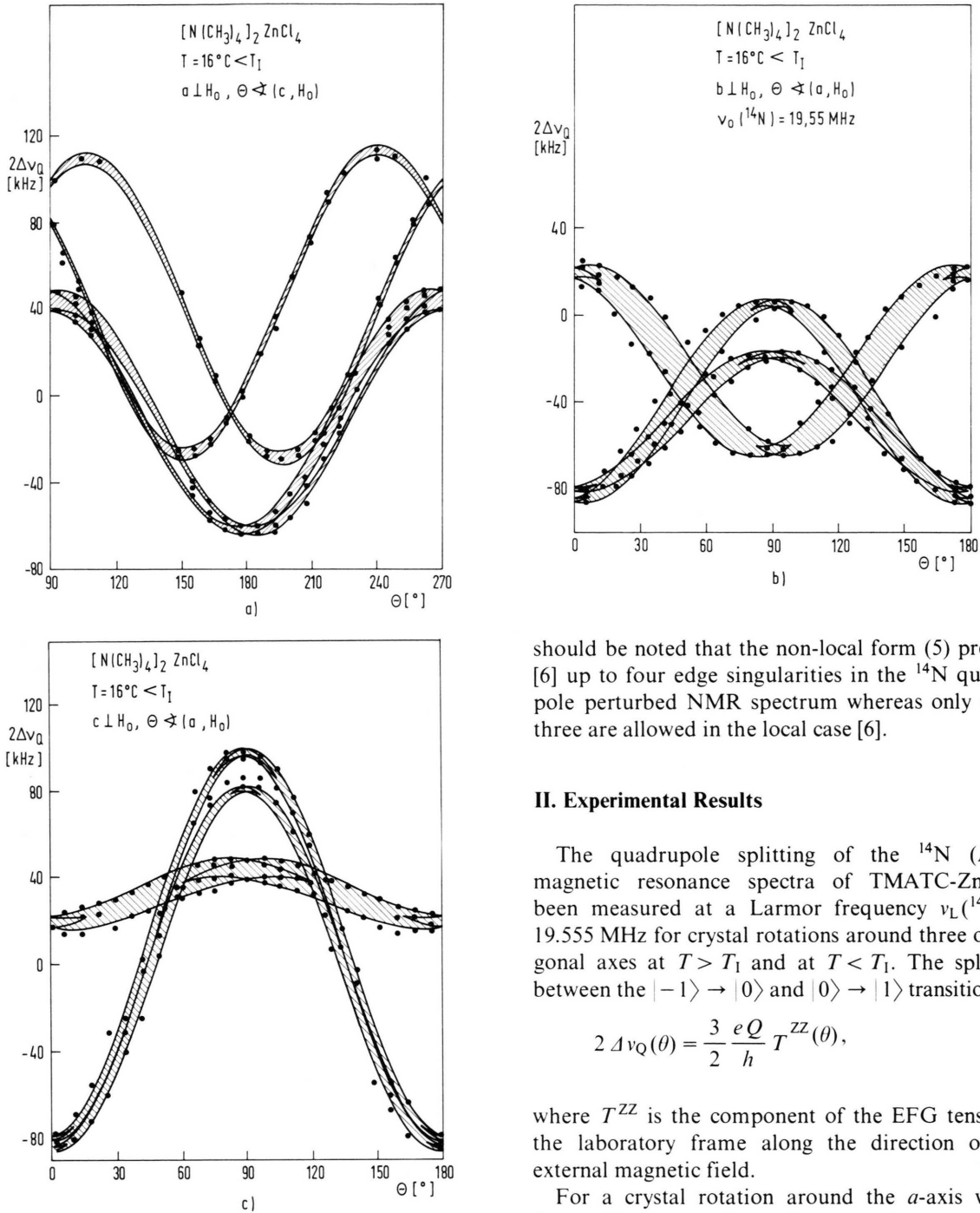
a)

b)

c)

Fig. 2. Angular dependence of the singularities $d(2\Delta v_Q)/d\Phi = 0$ in the ^{14}N spectra of TMATC-Zn in the incommensurate phase at $T = 16\,°C < T_I$. 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.

should be noted that the non-local form (5) predicts [6] up to four edge singularities in the ^{14}N quadrupole perturbed NMR spectrum whereas only up to three are allowed in the local case [6].

II. Experimental Results

The quadrupole splitting of the ^{14}N $(I = 1)$ magnetic resonance spectra of TMATC-Zn has been measured at a Larmor frequency $v_L(^{14}N) = 19.555$ MHz for crystal rotations around three orthogonal axes at $T > T_I$ and at $T < T_I$. The splitting between the $|-1\rangle \rightarrow |0\rangle$ and $|0\rangle \rightarrow |1\rangle$ transitions is

$$2\,\Delta v_Q(\theta) = \frac{3}{2}\frac{eQ}{h}T^{ZZ}(\theta),$$

(6)

where T^{ZZ} is the component of the EFG tensor in the laboratory frame along the direction of the external magnetic field.

For a crystal rotation around the a-axis where $\theta_a \measuredangle c, H_0$ one transforms from the laboratory to the crystal fixed a, b, c frame:

$$T^{ZZ}(\theta_a) = \tfrac{1}{2}(T^{bb} + T^{cc}) + \tfrac{1}{2}(T^{cc} - T^{bb})\cos 2\theta_a$$
$$+ T^{bc}\sin 2\theta_a.$$

(7a)

For rotations around the b and c-axes one similarly gets

$$T^{ZZ}(\theta_b) = \tfrac{1}{2}(T^{cc} + T^{aa}) \tag{7b}$$

$$+ \tfrac{1}{2}(T^{aa} - T^{cc})\cos 2\theta_b + T^{ac}\sin 2\theta_b,$$

$$T^{ZZ}(\theta_c) = \tfrac{1}{2}(T^{aa} + T^{bb}) \tag{7c}$$

$$+ \tfrac{1}{2}(T^{bb} - T^{aa})\cos 2\theta_c + T^{ab}\sin 2\theta_c.$$

In the I phase each of the above EFG tensor elements T^{aa}, T^{bb} etc. is described by expansion

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

$$\frac{\mathbf{T}_0(1)}{\text{kHz}} = \begin{vmatrix} 19 & 0 & 0 \\ 0 & 42 & 4 \\ 0 & 4 & -61 \end{vmatrix}; \quad (e^2qQ/h)_A = 41.3 \pm 0.65 \text{ kHz},$$
$$\eta_A = 0.375 \pm 0.005, \tag{8a}$$

$$\frac{\mathbf{T}_0(2)}{\text{kHz}} = \begin{vmatrix} 20 & 0 & 0 \\ 0 & 43 & -4 \\ 0 & -4 & -63 \end{vmatrix}; \quad (e^2qQ/h)_A = 41.3 \pm 0.65 \text{ kHz},$$
$$\eta_A = 0.375 \pm 0.005 \tag{8b}$$

$$\frac{\mathbf{T}_0(3)}{\text{kHz}} = \begin{vmatrix} -80 & 0 & 0 \\ 0 & 98 & -40 \\ 0 & -40 & -18 \end{vmatrix}; \quad (e^2qQ/h)_B = 60.65 \pm 4.65 \text{ kHz}$$
$$\eta_B = 0.485 \pm 0.035 \tag{8c}$$

$$\frac{\mathbf{T}_0(4)}{\text{kHz}} = \begin{vmatrix} -84 & 0 & 0 \\ 0 & 80 & 57 \\ 0 & 57 & 4 \end{vmatrix}; \quad (e^2qQ/h)_B = 60.65 \pm 4.65 \text{ kHz},$$
$$\eta_B = 0.485 \pm 0.035. \tag{8d}$$

(5). This results in an EFG tensor distribution since $\Phi(x)$ varies nearly continuously between 0 and 2π as one moves along the modulation direction. The NMR lineshape is now given by [6]

$$f(v) = \text{const}/\mathrm{d}v/\mathrm{d}x$$
$$= \text{const}/(\mathrm{d}v/\mathrm{d}\Phi)(\mathrm{d}\Phi/\mathrm{d}x). \tag{7d}$$

The angular dependence of the ¹⁴N quadrupole splitting $2\Delta v_Q$ for $T = 26\,°C > T_I$ is shown in Fig. 1a, b, c for rotations around the a, b and c crystal axes.

The results show the existence of four physically non-equivalent ¹⁴N EFG tensors which form two groups − A and B − of chemically non-equivalent ¹⁴N sites ($i = 1, 2 \rightarrow$ A, $i = 3, 4 \rightarrow$ B). The experimental error is about ± 2 kHz (Table 1).

In the I phase at $T = 16° < T_I$ $\mathbf{T}_0(i)$, $i = 1-4$ is not changed but $\mathbf{T}_{1''}(i)$, $\mathbf{T}_{2''}(i)$ and $\mathbf{T}_{2'}(i)$ are non-zero and can be determined [6] from the angular variation (Fig. 2a−c) of the singularities $\dfrac{\mathrm{d}\,2\Delta v_Q}{\mathrm{d}\Phi} = 0$ in the quasi-continuous ¹⁴N resonance frequency distribution. Since only the relative phase shift between the linear and the quadratic term is important, we put $\Phi_2 = 0$, $\Phi_1 \neq 0$. The results are collected in Table 2.

The results clearly show the presence of th two non-parallel out of phase components − perhaps rotation and displacement − of the modulation wave (4a) as there is a relative phase shift between the linear and the quadratic terms $\Phi_1 - \Phi_2 = 45°$

Table 2. ¹⁴N EFG tensors in kHz in the I phase of TMATC-Zn expressed in the crystal fixed a, b, c frame: $\mathbf{T}(x) = \mathbf{T}_0 + \mathbf{T}_{1''}\cos[\Phi(x) - \Phi_1] + \tfrac{1}{2}\mathbf{T}_{2'} + \tfrac{1}{2}\mathbf{T}_{2''}\cos 2[\Phi(x) - \Phi_2]$.

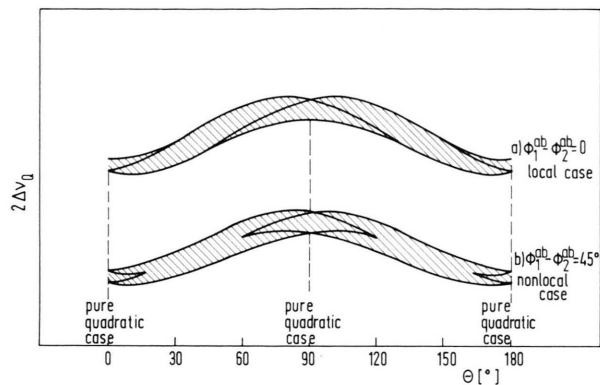|	$\mathbf{T}_{1''}$			$\mathbf{T}_{2'}$			$\mathbf{T}_{2''}$			Φ_1			$\Phi_2 = 0$
$i=1$	0	6	12	1	0	0	−5	0	0	0	45°	45°	
	6	0	0	0	3	4	0	9	4	45°	0	0	
	12	0	0	0	4	−2	0	4	4	45°	0	0	
$i=2$	0	6	12	−1	0	0	−5	0	0	0	45°	45°	
	6	0	0	0	1	−4	0	9	−4	45°	0	0	
	12	0	0	0	−4	2	0	−4	−4	45°	0	0	
$i=3$	0	5	5.5	0	0	0	2	0	0	0	45°	45°	
	5	0	0	0	1	6	0	−3	6	45°	0	0	
	5.5	0	0	0	6	−1	0	6	3	45°	0	0	
$i=4$	0	6	8	−2	0	0	−2	0	0	0	45°	45°	
	6	0	0	0	2	4	0	2	4	45°	0	0	
	8	0	0	0	4	3	0	4	−3	45°	0	0	

Fig. 3. Comparison between the angular dependences of the singularities in the ^{14}N spectra in the incommensurate phase according to the (a) "local" and (b) "non-local" models for $\Phi_1^{ab} - \Phi_2^{ab} = 45°$ and expansion (5) at $c \perp \boldsymbol{H}_0$, $\theta \not\prec (\boldsymbol{a}, \boldsymbol{H}_0)$.

and $\boldsymbol{T}_{2'} \neq \boldsymbol{T}_{2''}$. This is in sharp contrast to the predictions of the "local" model where the linear and quadratic terms have the same phase and where $\boldsymbol{T}_{2'} = \boldsymbol{T}_{2''}$.

The difference between the "local" and the "non-local" angular dependences is illustrated in Fig. 3 for $c \perp H_0$, $\theta \not\prec (\boldsymbol{a}, \boldsymbol{H}_0)$. The upper curve shows the "local" case where $\boldsymbol{\Phi}_1 - \boldsymbol{\Phi}_2 = 0$ and there are the singularities $d\, 2\Delta v_Q / d\Phi = 0$ close to the "pure" quadratic case, whereas the lower curve shows the "non-local" case for $\boldsymbol{\Phi}_1 - \boldsymbol{\Phi}_2 = 45°$ where four edge singularities are seen in the same region. The difference between the two cases is relatively small and one must be rather carefull if a proper fit and a proper determination of the EFG tensors should be made.

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