Temperature Dependence of the $^{127}$I-Nuclear Quadrupole Coupling in Tetramethylammonium-periodate (CH$_3$)$_4$NIO$_4$

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Tetramethylammonium-periodate shows $^{127}$I-NMR second order quadrupole splitting with negative temperature coefficients $\chi$ for the quadrupole coupling constants and a second order phase transition. From these measurements one can exclude the ratio $(r_{\text{cation}}/r_{\text{anion}}) > 1$ to be the origin of the anomalous temperature dependence in NH$_4$IO$_4$.

1. Introduction

With the identification of anomalous positive temperature coefficients $\chi$ for the quadrupole coupling constants $e^2 q Q/h$ and consequently for the electric field gradients in certain ammonium salts, for example NH$_4$ReO$_4$, ND$_4$ReO$_4$ and NH$_4$IO$_4$ [1–4], some attempts were made to explain these observations discussing the reorientational behaviour of NH$_4$, static effects or anomalous temperature dependence of the lattice parameter $a$, the basis length of the elementary cell [1, 5, 6]. The title compound (CH$_3$)$_4$NIO$_4$ was the first meta-periodate with a ratio $(r_{\text{cation}}/r_{\text{anion}}) > 1$ showing second order quadrupole effects in its solid state $^{127}$I-NMR spectra. In the temperature range 301 K < $T$ < 418 K we found a normal, but extremely large negative temperature coefficient $\chi$ for the $^{127}$I-quadrupole coupling constants [7]. This challenged us to further $^{127}$I-NMR measurements of (CH$_3$)$_4$NIO$_4$ at lower temperatures in order to exclude the ratio $(r_{\text{cation}}/r_{\text{anion}}) > 1$ to be responsible for anomalous quadrupole temperature coefficients.

2. Experimental

The $^{127}$I-NMR powder spectra of tetramethylammonium-periodate [8] measured with a Bruker FT-NMR CXP 200 spectrometer between 200 K and 300 K are depicted in Figure 1. The last spectrum at 300 K shows the typical second order $^{127}$I-NMR quadrupole splitting of the central $^{127}$I-NMR transi-

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tion (+1/2 $\leftrightarrow$ $-1/2$) with asymmetry parameter $\eta \rightarrow 0$. All other spectra with temperatures below $T = 296$ K have additional signals arising from a further quadrupole splitting.

### 3. Results and Discussion

When lowering the temperature, at least one of the quadrupole coupling constants increases because there are two possibilities in calculating the quadrupole splittings $\Delta v_n$:

- **Case A** with $\Delta v_1 = z^* \rightarrow z'$ and $\Delta v_2 = z \rightarrow z''$.
- **Case B** with $\Delta v_3 = z \rightarrow z'$ and $\Delta v_4 = z^* \rightarrow z''$.

By knowing the $^{127}$I-Larmor precession frequency $v_L$ at the field $B_0 = 4.698$ T and the measured values of $\Delta v_n$ for the respective temperatures the quadrupole coupling constants can be calculated for the asymmetry parameter $\eta = 0$. The results for $(\text{CH}_3)_4\text{NI}_04$ are shown in Table 1 and Fig. 2, which lead to the following conclusions:

(i) Independently of the two possible cases the diagram (Fig. 2) shows the appearance of a second phase at $T < 296$ K. The quadrupole coupling constants of this low temperature phase are in the order of 15 to 20 MHz and all $^{127}$I-quadrupole interactions of $(\text{CH}_3)_4\text{NI}_04$ have a normal temperature dependence with a negative temperature coefficient $\alpha$. This means that the condition $r((\text{CH}_3)_4\text{N}^+) > r(\text{IO}_7)$ does not cause anomalous temperature coefficients of the $^{127}$I-quadrupole coupling constants.

(ii) A second order phase transition is present independently of the two possible assignments, because there is a continuous change of the high temperature modification of the tetragonal crystal structure [8]. This will change the symmetry properties in the lattice and create two inequivalent positions of the iodine atoms.

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**Tab. 1.** Temperature dependence of second order $^{127}$I-NMR quadrupole splitting $\Delta v$ of $(\text{CH}_3)_4\text{NI}_04$. The quadrupole coupling constants $e^2qQ/h$ are calculated [9] with $\eta = 0$ for both cases A and B using $e^2qQ/h = 4\sqrt{2} |\Delta v_n| v_L$ ; $v_L = ^{127}$I-Larmor frequency at $B_0 = 4.698$ T.

<table>
<thead>
<tr>
<th>$T$ [K]</th>
<th>Case A</th>
<th></th>
<th>Case B</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta v_1$ [kHz]</td>
<td>$e^2qQ/h$ [MHz]</td>
<td>$\Delta v_2$ [kHz]</td>
<td>$e^2qQ/h$ [MHz]</td>
</tr>
<tr>
<td>300</td>
<td>$-$</td>
<td>$-$</td>
<td>$-$</td>
<td>$-$</td>
</tr>
<tr>
<td>296</td>
<td>$-$</td>
<td>$-$</td>
<td>$-$</td>
<td>$-$</td>
</tr>
<tr>
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<td>15.9</td>
<td>205.7</td>
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<td>227.7</td>
<td>17.1</td>
<td>280.8</td>
<td>19.0</td>
</tr>
</tbody>
</table>
(iii) An extrapolation of the known $e^2 q Q/h$-curve ($\triangle\triangle\triangle$) into the region $T < 300$ K (see Fig. 2) runs through the average values of the quadrupole coupling constants calculated from the two possible cases A and B. From our measurements it is impossible to decide, which of the two cases correctly describes the behaviour in the lattice, where obviously two sorts of distorted IO$_4^-$-tetrahedrons exist. With case B one of the IO$_4^-$-tetrahedra is provided with a small electric field gradient, which is independent of temperature (lower curve $\circ\circ\circ$). The other has a larger electric field gradient, which is temperature dependent. Consequently the IO$_4^-$-tetrahedron is more distorted. If case A prevails, one group of the IO$_4^-$-tetrahedrons changes its field gradient at the iodine atom in the same way as the high temperature modification. This can be seen in Fig. 2, where the $\triangle$-curve passes continuously into the lower $\square$-curve. For the other IO$_4^-$-tetrahedron one observes an insignificantly larger electric field gradient. In this preferred version there are smaller deviations in the lattice. Further studies of (CH$_3$)$_4$NI$_4$ together with another group [11] are in progress.

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