Iodine NQR and Phase Transitions in [N(CH₃)₄]₂ZnI₄*.

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Using a superregenerative NQR spectrometer, the temperature dependence of ¹²⁷I NQR spectra in [N(CH₃)₄]₂ZnI₄ was measured between 167 and 335 K. The measurements confirm two known structural phase transitions at 219 and 257.5 K. The correspondence between the distinct regions of iodine NQR spectra and the crystal structure is discussed. The relation of [N(CH₃)₄]₂ZnI₄ to the incommensurate family with the general formula X₂Y₂Z₄ and the high temperature (paraphase) crystal space group D₄h (Pmcn) is studied.

Key words: NQR, phase transitions, ferroelectric, crystal structure, displacement modulation.

1. Introduction

Tetramethylammonium-tetraiodozincate [N(CH₃)₄]₂ZnI₄ ([TMA]₂ZnI₄) belongs to the A₂BX₄ family, known by its incommensurate members and variety of phase transitions. Above ~260 K (Tc₁) the crystal is paraelectric and its structure is of K₂SO₄-II-type [1]. It belongs to the orthorhombic space group: D₄h (Pmcn) with 4 molecular units in the unit cell, which is usual for the high temperature structures of the family. Below ~220 K (Tc₂) the crystal changes to a less symmetric orthorhombic space group C₂ᵥ (Pbcn) and is ferroelectric [1, 2]. In this phase the structure can be interpreted as the room temperature structure (Pmcn) modulated by a static displacement wave along the b-direction with the wave-length equal to 2b. The unit cell is therefore doubled and contains 8 molecular units. Such a modulation is in contrast to the structure of most crystals belonging to the A₂BX₄ family, where the low temperature lattice modulation is along the pseudo-hexagonal c-axis. To the best of our knowledge, the only other example of modulation along the b-axis is with [N(CH₃)₄]₂CuBr₄ [3, 4].

The nature of the phase between Tc₁ and Tc₂ [1, 2] is not well understood. The absence of satellite reflections in x-ray scattering [1, 2] in spite of the fact that the Lifshitz invariant exists [5] seems to suggest that this phase is not a classical incommensurate phase as in the case of [N(CH₃)₄]₂ZnCl₄ [6]. Recent optical and DSC studies [1] as well as the ¹⁴N NMR study along with the application of Landau theory of phase transitions [5] indicate monoclinic symmetry of this case. In order to better understand different phases of this compound, the temperature dependence of the ¹²⁷I NQR spectra of the transition ±3/2 → ±1/2 was measured. At room temperature two resonance lines were detected. Their frequency ratio is practically 2:1, so it is very probably that they belong to the transitions ±5/2 → ±3/2 and ±3/2 → ±1/2 of the same ¹²⁷I nuclei. From the ratio 1.995 the corresponding EFG asymmetry parameter [8] can be estimated to be about 0.05.

2. Experimental

The measured sample was a single crystal of about 0.5 cm³. The r.f. coil was wound on the sample, which was protected by teflon tape. It was placed in a stream of cold (or warm) nitrogen gas in a thermally insulated case. In order to better understand different phases of this compound, the temperature dependence of the ¹²⁷I NQR spectra in [N(CH₃)₄]₂ZnI₄ was measured between 167 and 335 K. The measurements confirm two known structural phase transitions at 219 and 257.5 K. The correspondence between the distinct regions of iodine NQR spectra and the crystal structure is discussed. The relation of [N(CH₃)₄]₂ZnI₄ to the incommensurate family with the general formula X₂Y₂Z₄ and the high temperature (paraphase) crystal space group D₄h (Pmcn) is studied.

Key words: NQR, phase transitions, ferroelectric, crystal structure, displacement modulation.

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The temperature dependence of the $^{127}$I NQR spectrum is shown in Figure 1. The transition temperatures were determined to be $(219 \pm 1)$ K and $(257.5 \pm 1)$ K.

3. Results and Discussion

Like most members of the $\text{A}_2\text{BX}_4$ family, $(\text{TMA})_2\text{ZnI}_4$ has the high temperature structure $\text{Pmcn}$ [1], which is called the basic structure. Viewed along the $c$ axis, such a structure is apparently pseudo-hexagonal [7]. The low temperature structures of the family can be expressed as deviations from the $\text{Pmcn}$ structure. In $(\text{TMA})_2\text{ZnI}_4$ the $\text{Pmcn}$ unit cell [1,7] contains four molecular units. The four $[\text{ZnI}_4]^{2-}$ tetrahedra are chemically equivalent (see Figure 2).

Each tetrahedron is intersected by a mirror plane such that two I atoms, called $I_1$ and $I_2$, and the central Zn atom lie in this plane. The remaining two I atoms, $I_3$ and $I_4$, lie symmetrically at the opposite sides of the plane. In such a case we obtain three NQR lines for each quadrupole transition ($\pm 3/2 \leftrightarrow \pm 1/2$ or $\pm 5/2 \leftrightarrow \pm 3/2$): one stronger line corresponding to the symmetrical pair $I_3$ and $I_4$, and two weaker lines, corresponding to $I_1$ and $I_2$.

The crystal was oriented with its $a$ axis parallel to the coil axis. Its mirror plane which is parallel to the $(b, c)$ plane and contains the pseudohexagonal axis $c$, was therefore orthogonal to the coil axis. In the above orientation, assuming the structure analogous to the ones of $\text{K}_2\text{SeO}_4$, $\text{Rb}_2\text{ZnCl}_4$, etc., no Zn–I bond is parallel to the coil axis and all the NQR signal intensities should be non-zero [8].

3.1 Phase I

Qualitatively, in the paraphase between $T_{c2}$ and 284 K three $^{127}$I NQR lines ($\pm 3/2 \leftrightarrow \pm 1/2$) appeared as expected. Surprisingly, only one strong line remains above 284 K. The two weaker lines disappear in the noise level. The reason for that could be the shortening of the relaxation time $T_2^*$ which is a measure of the duration of the free induction decay after the rf pulse. The superregenerative detection is not possible if $T_2^*$ becomes shorter than the inverse quench frequency of the superregenerative spectrometer (about 10 µs in this case). The torsional lattice vibrations and consequent broadening of the resonance line through the life time of quadrupole states are possible mechanism for the $T_2^*$ shortening, as was pointed out in [8].

With the temperature dependence of torsional lattice vibrations, we explain the temperature dependence of the $^{127}$I NQR frequencies in Phase I as follows. Slightly above $T_{c2}$, the $T_2^*$ values of two weak lines are just a little longer than the inverse of the
quench frequency, so the lines can be observed. These two $T^*_q$ values are temperature dependent and with increasing temperature both $T^*_q$ values further shorten. $T^*_q$ of the strong line is longer and is less temperature dependent. With the usual assumption that $[\text{ZnI}_4]^{2-}$ is rigid, such a situation is realized if the dominant torsional vibrations of the $[\text{ZnI}_4]^{2-}$ tetrahedra take place around the Zn–I bond corresponding to the strong spectral line. This bond is collinear with the principal $Z$ axis of the EFG tensor, which is almost axially symmetric (see the frequency ratio of the two transitions $\pm 5/2 \leftrightarrow \pm 3/2$ and $\pm 3/2 \leftrightarrow \pm 1/2$). Torsional vibrations around this axis leave the tensor almost unchanged and have little effect on quadrupole transitions which would shorten the corresponding $T^*_q$. On the other hand, this kind of vibrations has much more effect on the EFG tensors of the remaining three iodine atoms in the tetrahedron.

According to the Bayer theory [9], the torsional vibrations are also an important reason for the temperature dependence of the NQR lines. Table 1 shows that the strongest line at 273 K has also the smallest temperature coefficient, which is in accordance with the above explanation.

In Table 1 our tentative assignment of the observed lines is indicated as well. We suggest that the strongest rotational vibrations of the $[\text{ZnI}_4]^{2-}$ tetrahedron are those around the Zn–I$_1$ bond, so the strongest NQR signal belongs to the I$_1$ atom. In the isomorphous K$_2\text{SeO}_4$ crystal such a rotation takes part in the soft mode responsible for the transition from the paraphase to the incommensurate phase [10].

The lowest frequency line, ascribed to I$_3$ and I$_4$ seems to be somewhat stronger and persists to some degrees higher temperature than the upper weak line. However, the upper line I$_2$ is difficult to measure because it overlaps with the side-bands of the strong line I$_1$. It may be mentioned that similarly as here, also the isomorphous Rb$_2\text{ZnCl}_4$ and Rb$_2\text{ZnBr}_4$ crystals have the lowest frequency paraphase NQR line ascribed to the atoms Cl$_3$, Cl$_4$ (Br$_3$, Br$_4$). In those spectra, however, all the three paraphase lines have comparable intensity.

### 3.2 Phase II

This phase is monoclinic, with the unit cell containing 8 molecular units [1, 5]. It is supposed that the structure can be described by a displacement modulation of the basic structure. The modulation eliminates the previous mirror plane. The wave length of the displacement wave is twice the deformed basic unit cell length. Since the enthalpy change accompanying the transition is small [1] and there is no appreciable hysteresis, only a small structural rearrangement seems to take place. On approaching $T_{c2}$ from Phase I, the NQR signal from I$_1$ looses about 3/4 of its maximum intensity, in contrast to the weaker lines which are not so much affected. This can be explained by the effective axis of the torsional vibrations being no more collinear with the direction Zn–I$_1$. The atomic shifts

![Schematic diagram of the basic structure. The circles represent N(CH$_3$)$_4$ cations and the triangles $[\text{ZnI}_4]^{2-}$ tetrahedra.](image)

### Table 1. $^{127}$I NQR frequencies, intensities and temperature coefficients in the paraphase at 273 K.

<table>
<thead>
<tr>
<th>Atom</th>
<th>NQR frequency [MHz]</th>
<th>Temperature coef. [kHz/K]</th>
<th>$s/n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I$_1$</td>
<td>78.35</td>
<td>-4.5</td>
<td>19</td>
</tr>
<tr>
<td>I$_2$</td>
<td>78.90</td>
<td>-16</td>
<td>1</td>
</tr>
<tr>
<td>I$_3$, I$_4$</td>
<td>76.19</td>
<td>-8</td>
<td>2</td>
</tr>
</tbody>
</table>
caused by the soft mode torsional vibration remain frozen in the new structure below $T_{c2}$.

At the transition, the spectral line belonging to $I_3$ and $I_4$ splits into two lines which have strong temperature dependence. It is difficult to say if at $T_{c2}$ the splitting starts continuously from 0 or not; but 2.5 K below $T_{c2}$ the separation is quite large and easily measurable with the superregenerative spectrometer.

Within the resolution of our spectrometer, the temperature dependence of the remaining two lines seems to be continuous at $T_{c1}$. No splitting is noticed. The slopes, however, abruptly increase. The intensity of the line $I_1$ increases again as the sample temperature is lowered.

The quadrupole spectrum in Phase II (Fig. 1) indicates that only $I_3$ and $I_4$ feel two appreciably different electrostatic environments in the temperature region, which is reflected by the splitting of the corresponding line. The frozen in displacement wave leaves the positions of $I_1$ and $I_2$ apparently non-modulated (their NQR lines are not appreciably split). In the sequence of basic cells in the displacement wave, we suppose that only the position of the $I_3$, $I_4$ pair is appreciably modulated, as indicated on Figure 3a. This would mean that in the modulation wave the $[\text{ZnI}_4]^2-$ tetrahedra are symmetrically rotated around the connecting line $I_1$–$I_4$ (the mirror plane may change to a glide plane). We add that also a symmetrical modulation of the atoms $I_1$ and $I_2$ about the basic mirror plane is compatible with no splitting of the corresponding lines.

### 3.3 Phase III

In this phase, which is the ferroelectric phase, the Pmcn mirror plane vanishes and the unit cell contains double number of molecular units, the same as in Phase II. Therefore we obtain four chemically non-equivalent sites from any Pmcn non-mirror-plane site (line $I_3$, $I_4$ in Phase I) and two chemically nonequivalent sites from a mirror-plane site (lines $I_1$ and $I_2$ in Phase I). Indeed, a splitting of the lines $I_1$ and $I_2$ appears, which means that the corresponding positions become appreciably modulated. The modulation of the $I_3$, $I_4$ pair becomes asymmetric regarding the Pmcn mirror plane (Fig. 3b), causing further splitting of the Phase II doublet $I_3$, $I_4$.

### 4. Conclusions

$^{127}$I NQR is a sensitive and easy method for the detection of structural changes. But for the interpretation of the NQR spectra some additional structural information is usually desired. Unfortunately, only the data about the high- and the low-temperature phase crystal space groups were available for (TMA)$_2$ZnI$_4$. Accordingly, we had to assume some structural analogies between this compound and the other members of the family. Then it was possible to speculate about the form of structural changes from the behaviour of NQR spectrum. The $^{127}$I NQR spectra of the Phases II and III indicate that the atoms $I_3$, $I_4$ are most affected by the structural changes. The separations in the doublets $I_1$ and $I_2$ in Phase III are relatively small.

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