Iodine NQR and Phase Transitions in $[N(CH_3)_4]_2ZnI_4$*, [a]

J. Pirnat, J. Lužnik, and Z. Trontelj
Inst. of Mathematics, Physics and Mechanics and Physics Department,
University E. Kardelj of Ljubljana, Ljubljana, Yugoslavia

P. K. Kadaba
Department of Electrical Engineering, University of Kentucky, Lexington, U.S.A.

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Using a superregenerative NQR spectrometer, the temperature dependence of ^{127}I NQR spectra in $[N(CH_3)_4]_2ZnI_4$ 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 $[N(CH_3)_4]_2ZnI_4$ to the incommensurate family with the general formula X_2YZ_4 and the high temperature (paraphase) crystal space group D_{2h}^{16} (Pmcn) is studied.

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

1. Introduction

Tetramethylammonium-tetraiodozincate $[N(CH_3)_4]_2ZnI_4$ $[(TMA)_2ZnI_4]$ belongs to the A_2BX_4 family, known by its incommensurate members and variety of phase transitions. Above ~260 K (T_{c2}) the crystal is paraelectric and its structure is of K_2SO_4-II-type [1]. It belongs to the orthorhombic space group: D_{2h}^{16} (Pmcn) with 4 molecular units in the unit cell, which is usual for the high temperature structures of the family. Below ~220 K (T_{c1}) the crystal belongs to a less symmetric orthorhombic space group C_{2v}^5 ($Pbc2_1$) 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 A_2BX_4 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 $[N(CH_3)_4]_2CuBr_4$ [3, 4].

The nature of the phase between T_{c1} and T_{c2} [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 $[N(CH_3)_4]_2ZnCl_4$ [6]. Recent optical and DSC studies [1] as well as the ^{14}N 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 ^{127}I NQR spectra of the transition $\pm 3/2 \leftrightarrow \pm 1/2$ 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 $\pm 5/2 \leftrightarrow \pm 3/2$ and $\pm 3/2 \leftrightarrow \pm 1/2$ of the same ^{127}I 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 cm^3. 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 tube with a Cu-const. thermocouple to measure the temperature with an accuracy of ±1 K. A commercial superregenerative NQR spectrometer Wilks NQR-1A was used for the NQR measurements, and a Tektronix Spectrum Analyzer 7L12 for the central frequency determination. The crystal was oriented with its ***a*** axis parallel to the coil axis and its ***b*** axis approximately parallel to the Zeeman modulation coil axis. The tem-

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Reprint requests to Dr. Janez Pirnat, IMFM, P.O. Box 28 (Jadranska 19), 61111 Ljubljana, Yugoslavia.

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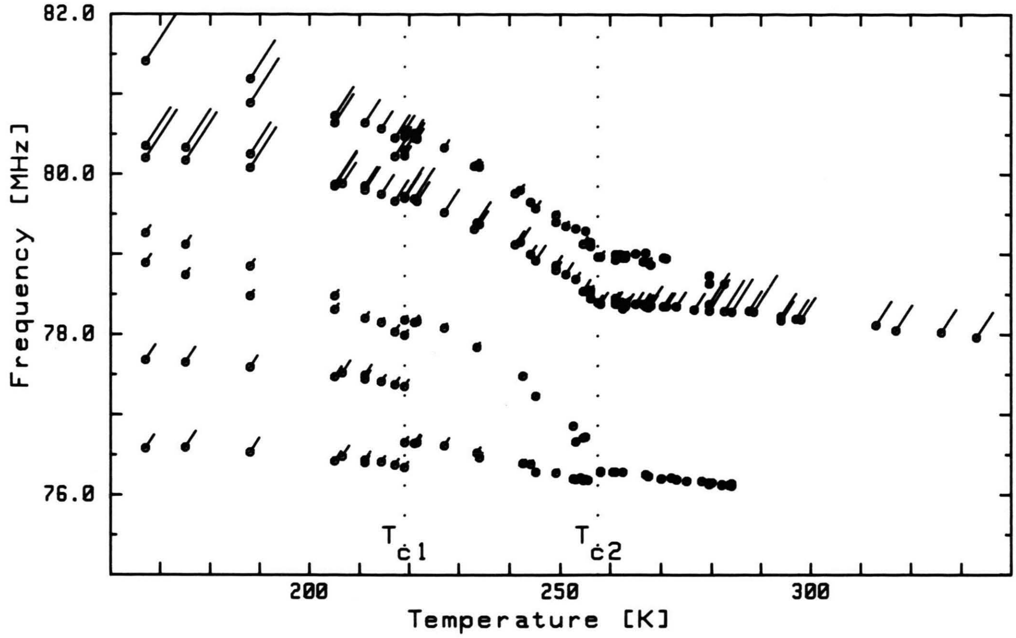

Fig. 1. Temperature dependence of the ^{127}I NQR spectrum. The length of the sign (⌀) is proportional to the spectral intensity.

perature dependence of the NQR frequencies is shown in Figure 1. The transition temperatures were determined to be (219 ± 1) K and (257.5 ± 1) K.

3. Results and Discussion

Like most members of the A_2BX_4 family, $(TMA)_2ZnI_4$ has the high temperature structure Pmcn [1], which is called the basic structure. Viewed along the ***c*** axis, such a structure is apparently pseudohexagonal [7]. The low temperature structures of the family can be expressed as deviations from the Pmcn structure. In $(TMA)_2ZnI_4$ the Pmcn unit cell [1, 7] contains four molecular units. The four $[ZnI_4]^{2-}$ 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 K_2SeO_4, Rb_2ZnCl_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 then the inverse of the quench frequency, so the lines can be observed. These two T_2^* values are temperature dependent and with increasing temperature both T_2^* values further shorten. T_2^* of the strong line is longer and is less temperature dependent. With the usual assumption that $[ZnI_4]^{2-}$ is rigid, such a situation is realized if the dominant torsional vibrations of the $[ZnI_4]^{2-}$ tetrahedra take place around the Zn–I bond corresponding to the strong spectral line. This bond is collinear with the principal $\boldsymbol{Z}$ 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_2^*. 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 $[ZnI_4]^{2-}$ tetrahedron are those around the $Zn-I_1$ bond, so the strongest NQR signal belongs to the I_1 atom. In the isomorphous K_2SeO_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_2ZnCl_4 and Rb_2ZnBr_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

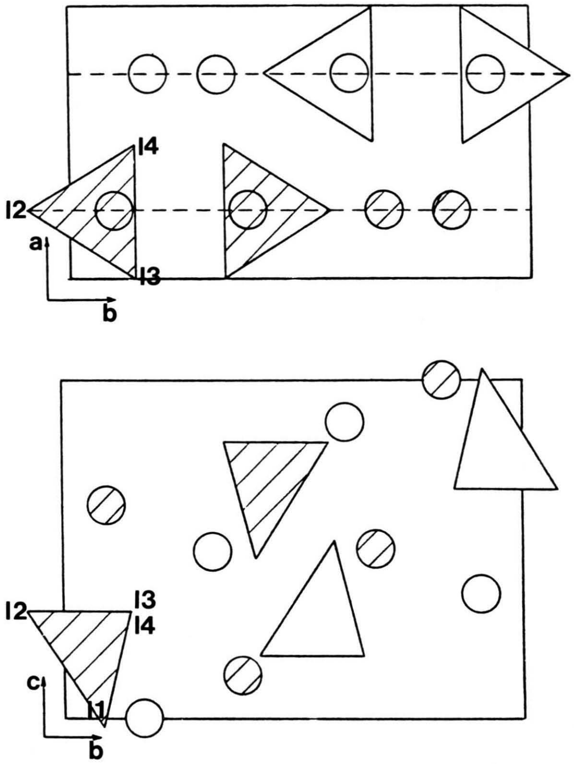

Fig. 2. Schematic diagram of the basic structure. The circles represent $N(CH_3)_4^+$ cations and the triangles $[ZnI_4]^{2-}$ tetrahedra.

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

Atom	NQR frequency [MHz]	Temperature coef. [kHz/K]	s/n
I_1	78.35	– 4.5	19
I_2	78.90	–16	1
I_3, I_4	76.19	– 8	2

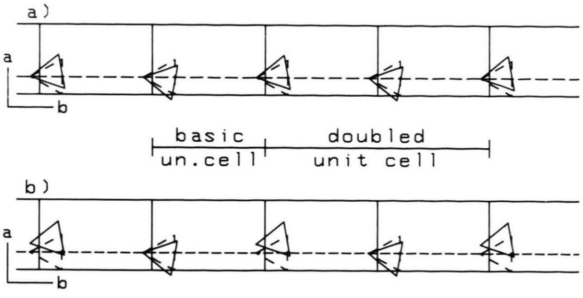

Fig. 3. Schematic representation of a possible displacement modulation of the $[ZnI_4]^{2-}$ tetrahedra a) in Phase II and b) in Phase III.

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 $[ZnI_4]^{2-}$ tetrahedra are symmetrically rotated around the connecting line I_1-I_2 (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 nonequivalent 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 $(TMA)_2ZnI_4$. 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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