

Incommensurate Modulation of EFG in ThX_4 ($\text{X}=\text{Cl}, \text{Br}$)¹

J. Pirnat, V. Jazbinšek

IMFM, Univ. E. Kardelj of Ljubljana

P.O. Box 28, 61111 Ljubljana

YUGOSLAVIA

Contents

I. Introduction	148
II. Incommensurate Modulation of Basic Structure and EFG	148
III. Incommensurate Modulation of Halogene NQR	150
IV. Conclusion	151
V. References	151

The correlation between the atomic displacements in the incommensurate phase and the corresponding temperature dependence of the NQR spectra distribution was calculated. The calculations qualitatively explain the experimentally obtained temperature dependence.

I. Introduction

β -form of ThX_4 compounds ($\text{X}=\text{Cl}, \text{Br}$) has crystal structure, shown on Fig. 1 and belonging to space group D_{4h}^{19} ($I4/amd$) (1,2). By both halogenides a phase transition to an incommensurate phase was detected at lower temperature (3). In the new phase a displacive modulation of halogene positions is superimposed on the paraphase structure which is called the basic structure. The displacement wave is incommensurate with the high temperature crystal structure ($\vec{q}_i = \vec{c}(1-\delta)/3$). The electric field gradient (EFG) tensor felt by the nuclei which were equipositional in the paraphase, becomes mod-

ulated congruently with the displacement wave. In the following the correlation between the atomic displacements in the incommensurate phase and the corresponding nuclear quadrupole resonance (NQR) line distribution (because of the modulation of the EFG tensor) is discussed.

II. Incommensurate Modulation of Basic Structure and EFG

In the ThX_4 structure below T_i the static ionic displacements $\vec{u}_{n\varphi}$ from the paraphase positions can be expressed in the single-plane-wave approximation as (4)

$$\vec{u}_{n\varphi} = A\{\vec{e}_1|n\}\cos[\epsilon(n)K + \varphi]$$

$$\epsilon(n) = \begin{cases} -1, & \text{if } 0 \leq n \leq 5 \\ 1, & \text{if } 6 \leq n \leq 10. \end{cases} \quad (1)$$

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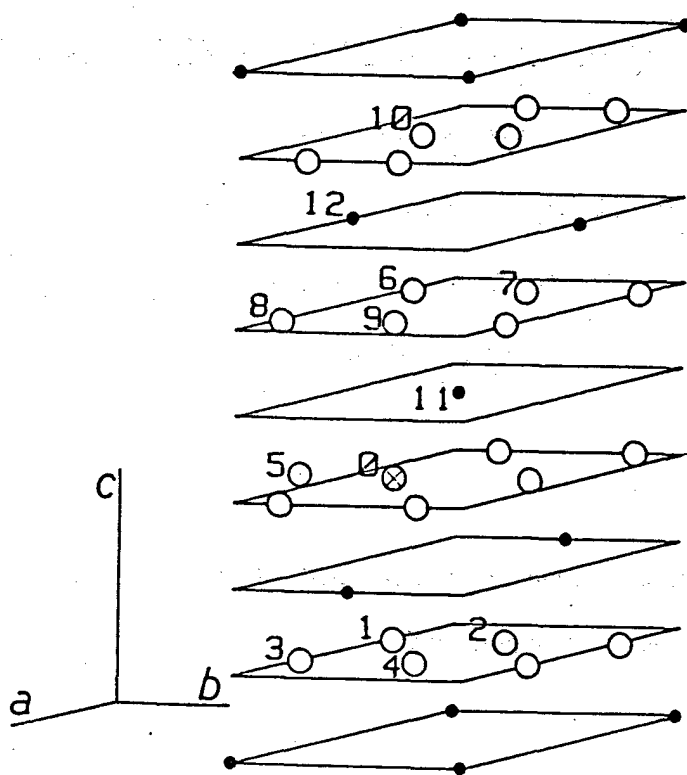


Figure 1: Schematic representation of ThX_4 structure (\bullet Th, \circ X). For the sake of clarity the unit cell is cut into slices and c axis is elongated by a factor of 3.

Number n counts the ionic sites in the paraphase unit cell ($0 \leq n \leq N$) whereas the modulation phase angle φ rises in equal steps (incommensurate with 2π) from one cell to another along the modulation wave. \vec{e}_1 is $3N$ dimensional vector describing the displacements in the unit cell for a particular normal vibration compatible with the soft mode (see Fig. 2). Its projection $\{\vec{e}_1|n\}$ describes only the displacement of the atom n . The phase shift $\epsilon(n)K$ having the absolute value approximately 20 deg. (4) is negative for one half of the unit cell ($z < 1/2$, see Figs. 1 and 2) and positive for the other half. The displacement amplitude A is the same for all the halogene atoms regardless of the displacement direction (x or y).

We have defined the function $\epsilon(n)$ only for 11 atoms X which represent the environment of the chosen atom X_0 where the EFG tensor is to be calculated (see Fig. 1). Within this environment there are also two atoms Th, however they are not shifted. Our assumption is that more distant atoms do not contribute to the EFG shift at the chosen site appreciably. When we translate our conformation of

Table 1: Modulation Parameters

atom	0	1	2	3	4	5	6
ampl.	Ax	-Ay	-Ay	Ay	Ay	-Ax	-Ay
ph. shift	K	K	K	K	K	K	-K
atom	7	8	9	10	11	12	
ampl.	-Ay	Ay	Ay	Ax	0	0	
ph. shift	-K	-K	-K	-K	0	0	

$K \sim 20$ deg.

eleven atoms X and two atoms Th along the modulation wave, the probe atom X_0 can sense all the possible EFG tensors that can occur. For our calculations we have taken into account the modulation parameters shown in Table 1.

Because of the nonlinear dependence of a chosen EFG component V on coordinates, the modulation of this component in a displacively modulated structure can be written in the form of a series (5)

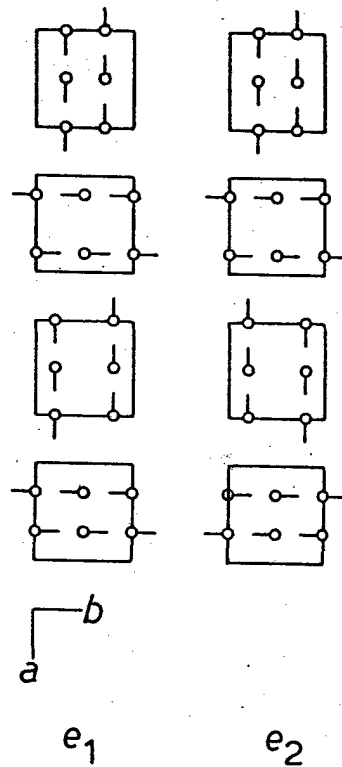


Figure 2: Vibration modes compatible with the soft mode (4). Four slices of the same unit cell with X atoms at $z = 1/8, 3/8, 5/8, 7/8$ are shown.

$$\begin{aligned}
 V &= V^{(0)} + \text{Re}[V^{(1)} \times \exp(i\varphi) + V^{(2)} \times \\
 &\quad \exp(2i\varphi) + V^{(3)} \times \exp(3i\varphi) + \dots] \\
 V^{(0)} &= V_0 + 1/4 \times \sum_{j,n} [A_{jn}^2 - 2A_j A_{jn} \times \\
 &\quad \cos(\phi_j - \phi_{jn}) + A_j^2] \partial^2 V / \partial x_{jn}^2 + \\
 &\quad 1/2 \times \sum_{j,k>j,n} [A_{jn} A_{kn} \times \cos(\phi_{jn} - \phi_{kn}) + \\
 &\quad A_j A_k \times \cos(\phi_j - \phi_k) - A_j A_{kn} \times \cos(\phi_j - \phi_{kn}) \\
 &\quad - A_k A_{jn} \times \cos(\phi_k - \phi_{jn})] \partial^2 V / \partial x_{jn} \partial x_{kn} + \dots \\
 V^{(1)} &= \sum_{j,n} [A_{jn} \times \exp(i\phi_{jn}) - A_j \times \exp(i\phi_j)] \partial V / \partial x_{jn} + \dots \\
 V^{(2)} &= 1/4 \times \sum_{j,n} \{A_{jn}^2 \times \exp(2i\phi_{jn}) - \\
 &\quad 2A_j A_{jn} \times \exp[i(\phi_j + \phi_{jn})] + A_j^2 \times \exp(2i\phi_j)\} \\
 &\quad \partial^2 V / \partial x_{jn}^2 + 1/2 \times \sum_{j,k>j,n} \{A_{jn} A_{kn} \times \\
 &\quad \exp[i(\phi_{jn} + \phi_{kn})] + A_j A_k \times
 \end{aligned}
 \tag{2}$$

$$\begin{aligned}
 &\exp[i(\phi_j + \phi_k)] - A_j A_{kn} \times \exp[i(\phi_j + \phi_{kn})] - \\
 &\quad A_k A_{jn} \times \exp[i(\phi_k + \phi_{jn})] \} \partial^2 V / \partial x_{jn} \partial x_{kn} + \dots
 \end{aligned}$$

Here x_{jn} , A_{jn} and ϕ_{jn} are the j -th coordinate, amplitude and phase shift respectively ($j=1,2,3$), of surrounding atom n ; x_j , A_j and ϕ_j are the j -th coordinate, amplitude and phase shift of the resonant atom.

III. Incommensurate Modulation of Halogene NQR

In general, the calculation of the halogene NQR frequency modulation from the modulation of the EFG tensor would be a tedious task because it would require a diagonalization of EFG at every different modulation phase angle. To simplify the calculation of NQR in the modulated structure, several assumptions were made. The EFG tensor is imagined as being composed of the chemical bond contribution and a much smaller part coming from the surrounding atoms approximated by point charges. The chemical bond part of the EFG tensor is assumed to be axially symmetric, the symmetry axis being parallel to the

connective line unit vector $\overrightarrow{[X - Th]} / |X - Th| = \vec{r}$. The displacement wave is assumed to affect only the minor part of the EFG- $q_{p.ch.}$. With these assumptions the modulated tensor remains almost axially symmetric and it can be easily shown that the NQR frequency is most sensitive to the changes of the greatest EFG eigenvalue. Up to the second order the frequency shift $\delta\nu$ is proportional to the shift of the EFG eigenvalue along the approximate principal axis which coincides with \vec{r} . The "projection" of the EFG shift in the crystal coordinate system (point charge part) to the EFG eigenvalue along \vec{r} is obtained by the corresponding rotation of the coordinate system (6):

$$\delta\nu_Q \sim \delta q_{p.ch.} \sim \left\{ \left[\begin{array}{ccc} \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ r_x & r_y & r_z \end{array} \right] \left[\begin{array}{ccc} \delta V_{xx} & \delta V_{xy} & \delta V_{xz} \\ \delta V_{yx} & \delta V_{yy} & \delta V_{yz} \\ \delta V_{zx} & \delta V_{zy} & \delta V_{zz} \end{array} \right] \left[\begin{array}{c} \cdot \\ \cdot \\ r_x \\ \cdot \\ \cdot \\ r_y \\ \cdot \\ \cdot \\ r_z \end{array} \right] \right\}_{zz} \quad (3)$$

$$= r_x^2 \delta V_{xx} + r_y^2 \delta V_{yy} + r_z^2 \delta V_{zz} + 2r_x r_y \delta V_{xy} + 2r_y r_z \delta V_{yz} + 2r_x r_z \delta V_{xz}.$$

The resulting NQR modulation obtained by the use of Eq. 3 is compared to the one obtained by the exact diagonalisation of the modulated EFG tensor on Fig. 3. The agreement improves with the ratio of the nonmodulated axially symmetric part to the modulated part.

In the modulated structure δV_{jk} are functions of the phase angle, φ , so the frequency distribution of the NQR line intensity is proportional to

$$\sigma I_{\nu_Q} / \sigma\nu \sim (\sigma\nu_Q / \sigma\varphi)_{1\nu}^{-1} \sim (\sigma q_{p.ch.} / \sigma\varphi)_{1\nu}^{-1}. \quad (4)$$

The dependence of the line shape on the displacement modulation amplitude is shown on Fig. 4. The proportionality factor was not determined because of unknown Sternheimer shielding factor (7) for the case of the point charge EFG shift superimposed on the chemical bond EFG.

If one admits the temperature dependence of the modulation amplitude (3)

$$A \sim (T_i - T)^{1/3}, \quad (5)$$

then the calculated temperature dependence of the halogene NQR line shape can be qualitatively compared to the experimental ones from Ref. 3. Figure

5 shows that after subtracting the smooth temperature dependence extrapolated from the paraphase, experiments approximately agree with theory. The agreement is better in the case of ThCl_4 except far away from the incommensurate transition temperature, where the plane-wave approximation is no longer valid.

IV. Conclusion

Theoretical temperature dependence of the edge singularities qualitatively follows the experimental points (3). Our results do not differ much from the expectations in ref. 3 on the basis of the local displacements is zero. Therefore our model predicts the appearance of only two edge singularities as the former model. The only appreciable difference of the results of our model in the present case is, that the local model expects one of the edge singularities to remain unshifted whereas our model brings about shifts of both singularities.

Our calculations offer us a possibility of exploring and comparing how different displacement modulation parameters influence the NQR frequency modulation.

V. References

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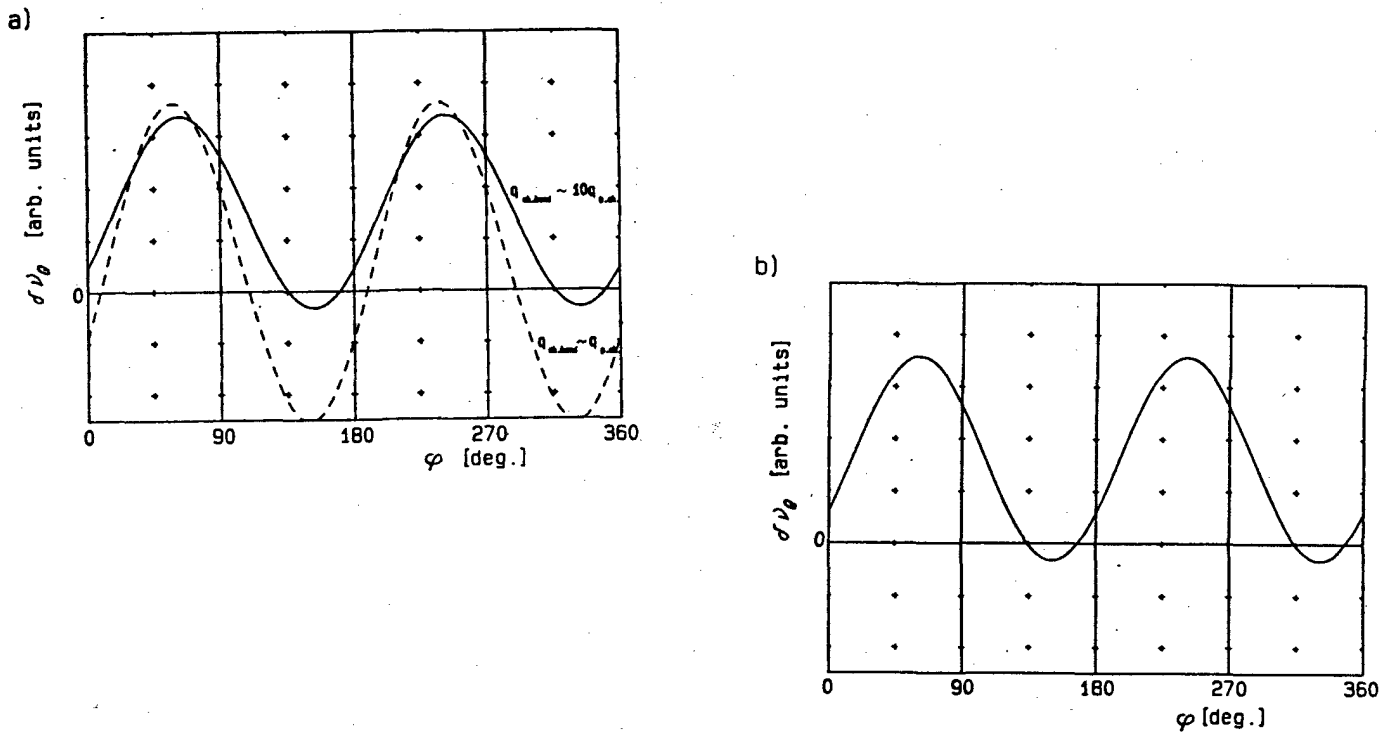


Figure 3: Comparison of NQR modulation obtained by the exact diagonalization of the modulated EFG tensor (diagram a: by the solid curve the constant part of the EFG tensor is 10 times stronger than by the dotted curve) to the one obtained by the approximation (3) (diagram b).

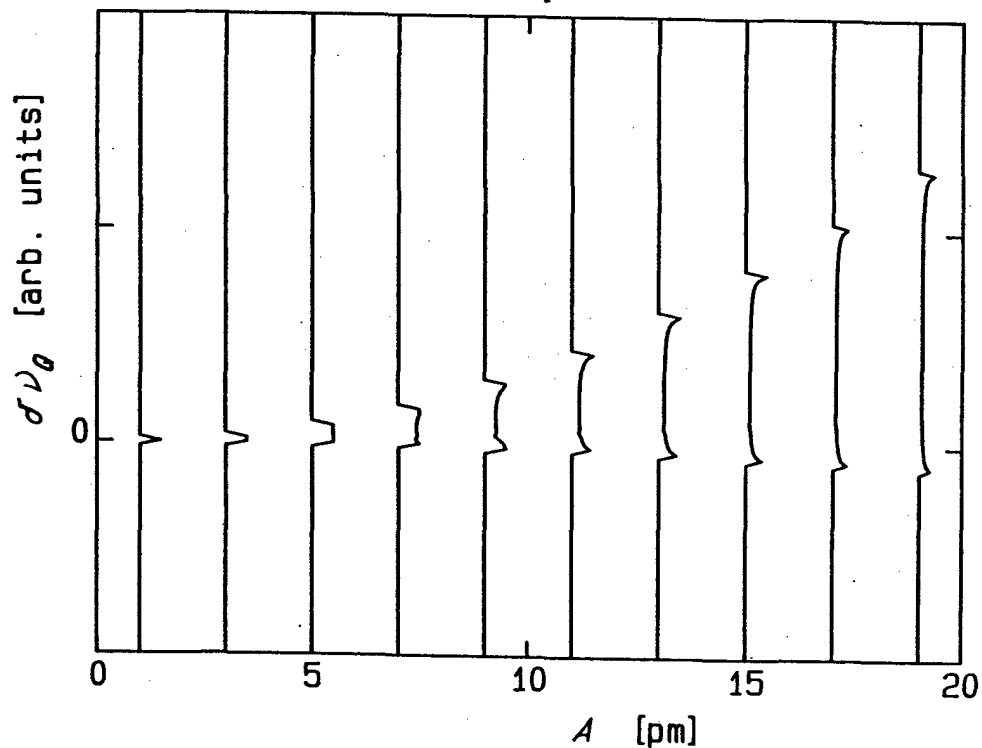


Figure 4: Influence of the amplitude of the displacement modulation on the halogen NQR line shape.

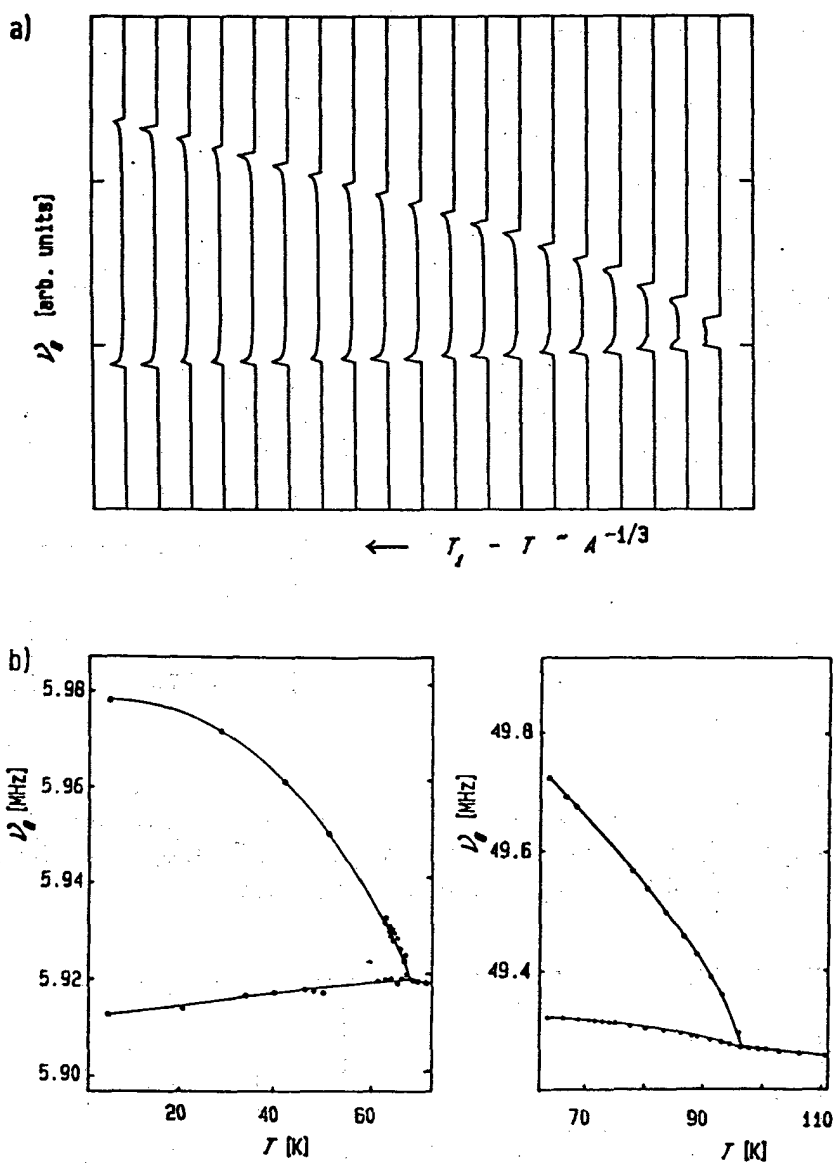


Figure 5: Comparison of the theoretical temperature dependence of the halogene NQR line shape (a) to the experimental results after Ref. 3 (b).