

CHLORINE NUCLEAR QUADRUPOLE RESONANCE  
AND HIGH TEMPERATURE PHASE TRANSITION IN  $\text{NaClO}_3$ \*

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*Abstract:* From Raman and dielectric measurements on  $\text{NaClO}_3$  a solid-to-solid phase transition seems possible with the extrapolated transition temperature above the melting point (537 K) at normal pressure. By measuring the  $^{35}\text{Cl}$  nuclear quadrupole resonance as a function of temperature and using the Bayer theory we followed the temperature dependence of the chlorate ion's torsional frequencies. Comparison with the Raman data shows that these frequencies do not correspond to the presumptive soft mode, appearing in the Raman measurements.

### 1. Introduction

Low frequency dielectric measurements (1 kHz)<sup>1)</sup> and Raman measurements<sup>2)</sup> on  $\text{NaClO}_3$  monocrystal show some anomalies characteristic for a solid-to-solid phase transition, which would occur slightly above the melting point. In order to investigate torsional frequencies of the  $\text{ClO}_3^-$  ion we measured nuclear quadrupole resonance (NQR) of the  $^{35}\text{Cl}$  at high temperatures up to the melting point (537 K). Our measurements are an extension of the previously reported data at lower temperatures<sup>3, 4, 5, 6)</sup>.

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$\text{NaClO}_3$  crystal has cubic symmetry with the space group  $T^4 (P2_13)^{71}$ . It has four formula units per unit cell (Fig. 1). Since all chlorine sites in the unit cell are equivalent only one  $^{35}\text{Cl}$  NQR frequency is observed. The electric field gradient (EFG) at Cl site is due mainly to the electric charge distribution inside the  $\text{ClO}_3^-$  group because of the rapid decreasing of EFG with increasing distance from its origin.

At nonzero temperatures thermal vibrations in the crystal very often average the EFG felt by the quadrupolar nucleus to a lower value. The Bayer theory takes into account this averaging when calculating the temperature dependence of NQR frequency. For an axially symmetric EFG the following equation is obtained

$$\nu_q = \nu_0 \left[ 1 - \frac{3h}{8\pi^2} \sum_i \frac{1}{f_i A_i} \left( \frac{1}{2} + \frac{1}{\exp(hf_i/kT) - 1} \right) \right]. \quad (1)$$

Here  $\nu_q$  and  $\nu_0$  are quadrupole frequencies for vibrating and rigid lattice, resp.,  $f_i$  the ground frequency of the  $i$ th torsional mode around  $x$  or  $y$  axis of the EFG with an axial symmetry around  $z$  axis,  $A_i$  the corresponding moment of inertia,  $T$  absolute temperature,  $h$  Planck constant and  $k$  Boltzmann constant. The summation is over all normal torsional modes, which do not conserve the symmetry axis of the EFG.

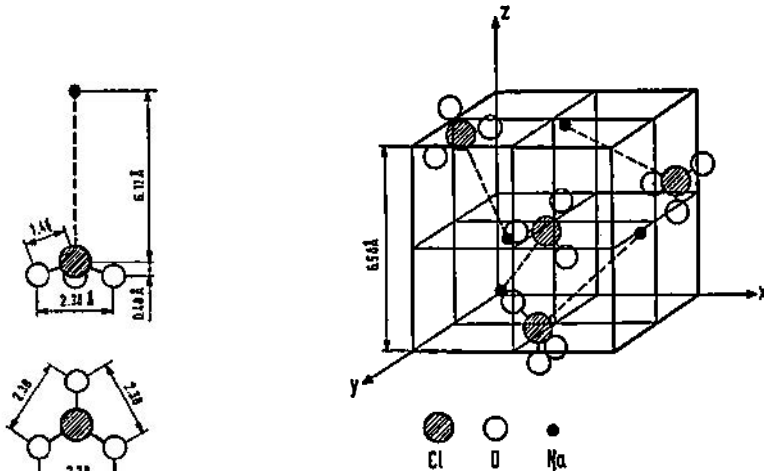


Fig. 1. Crystal structure of  $\text{NaClO}_3$ .

The EFG tensor has in the  $\text{ClO}_3^-$  group its principal  $z$  axis along the 3-fold symmetry axis; so the EFG is axially symmetric assuming that the farther environment does not contribute to the EFG. The moments of inertia of the  $\text{ClO}_3^-$  pyramid around the two axes, perpendicular to the 3-fold axis and passing through the centre of mass, are almost equal (within 1.5 %). One can expect that the corresponding

torsional frequencies are close to each other also. If we assume that torsional vibrations of a rigid chlorate ion only contribute to the averaging of the EFG at chlorine site, Equ. (1) becomes

$$\nu_q = \nu_0 \left[ 1 - 2 \frac{3}{8\pi^2 f_t A_t} \left( \frac{1}{2} + \frac{1}{\exp(hf_t/kT) - 1} \right) \right], \quad (2)$$

where the sum consists only of two equal contributions with the same average torsional frequency  $f_t$  around  $x$  or  $y$  axis, and the same average moment of inertia  $A_t$ . This equation has been proved at lower temperatures by previous NQR measurements<sup>4, 5, 6</sup>.

## 2. Results and discussion

All data were obtained with a commercial superregenerative spectrometer Wilks NQR-1A combined with a home made high temperature cell. Temperature measured with a copper-constantan thermocouple is accurate to  $\pm 1$  K. Frequency markers provided by Measurements Standard Signal Generator Model 80 were recorded together with the  $^{35}\text{Cl}$  NQR signal. The frequency of the signal generator was measured with the Hewlett-Packard 5327 C Frequency Counter to about 0.07 %, as obtained from the scattering of the measured points. The test tube in a RF coil contained approximately  $3 \text{ cm}^3$  of powder sample. The  $s : n$  ratio at room temperature was close to 100 : 1 and it fell down to 10 : 1 near the melting point.

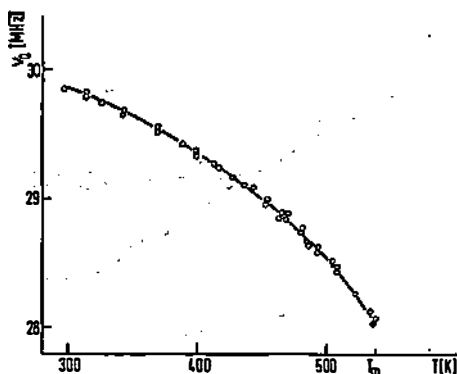


Fig. 2.  $^{35}\text{Cl}$  NQR frequency vs. temperature in  $\text{NaClO}_3$ .

The resulting temperature dependence of the  $^{35}\text{Cl}$  NQR frequency is shown on Fig. 2. The average moment of inertia  $A_t$  of the  $\text{ClO}_3^-$  ion for the rotations around the axis, perpendicular to the 3-fold axis, is  $8.25 \cdot 10^{-39} \text{ gcm}^2$ . Taking for  $\nu_0$  the extrapolated value 30.630 MHz, as in reference<sup>6</sup>), one can solve the

equation (2) for  $f_t$  with an iteration method. The temperature dependence of  $f_t$  shown in Fig. 3 was obtained. Results of the Raman measurements<sup>2)</sup> are in good agreement from room temperature up to 440 K.

The extensive Raman measurements on  $\text{NaClO}_3$  by Hartwig et al.<sup>9)</sup> give us opportunity to test whether the phonons which would correspond to our average torsional frequency of  $131 \text{ cm}^{-1}$  at room temperature, have the expected symmetry properties. According to the group theory, the torsional oscillations of the  $\text{ClO}_3$  ion which influence the chlorine NQR frequency should be present in five modes of crystal vibration: four of F type (two longitudinal-optical and two transversal-optical) and one of E type. If we assume that the torsional coefficient around 3-fold axis is the same as around  $x$  or  $y$  axis, we would expect from the ratio of the momenta of inertia of the chlorate ion near  $97 \text{ cm}^{-1}$  two Raman frequencies belonging to the modes of F type (again differing from each other by their polarization only) and one belonging to the mode of A type. These phonons are related to the torsional oscillations around the 3-fold symmetry axis. Experimental results<sup>9)</sup> agree with the predictions of group theory except in two points. First, the listed<sup>9)</sup> A phonon at  $134 \text{ cm}^{-1}$  does not incorporate into the scheme (it should correspond

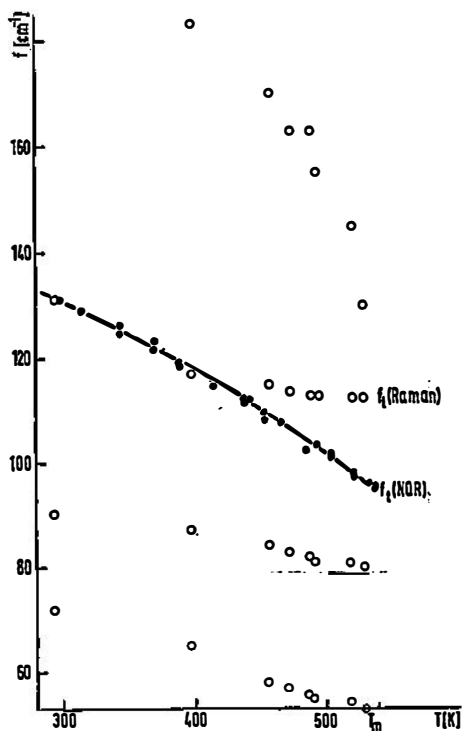


Fig. 3. Temperature dependence of the sodium chlorate Raman frequencies and torsional frequency, obtained from the NQR measurements in this sample.

to nontorsional oscillation of  $\text{ClO}_3^-$  ion). Second, an A phonon is missing near  $97 \text{ cm}^{-1}$ . But on the Raman spectra shown in reference<sup>9)</sup>, Fig. 3b, there is a perceivable peak between  $90$  and  $100 \text{ cm}^{-1}$ , which would belong to A symmetry while the authors do not mention why it was excluded from their list of optical phonons in  $\text{NaClO}_3$ . These points should be discussed, maybe after repeating the Raman measurements with special emphasis on them.

Then it might be easier to identify the normal oscillation to which the possible soft mode at  $186 \text{ cm}^{-1}$  (room temperature)<sup>2)</sup> belongs, and to predict the possibility of a phase transition.

Above  $440 \text{ K}$  our calculated torsional frequencies lie below those obtained from the Raman measurements<sup>2)</sup>. Actually our data from  $300 \text{ K}$  to  $537 \text{ K}$  obey the empirical equation

$$f_i^2 = 2.97 \frac{\text{cm}^{-2}}{\text{K}} (808 \text{ K} - T), \quad (3)$$

as shown in Fig. 4. The discrepancy near the melting point is not unusual for this type of solids. There are a few possible explanations. Sometimes it is explained by increasing influence of the vibrations in the covalent bonds which are directly causing the EFG at the resonating nucleus site. In our case these frequencies are rather high, i. e. above  $482 \text{ cm}^{-1}$ <sup>9)</sup>, and it was shown by Kushida<sup>10)</sup> that

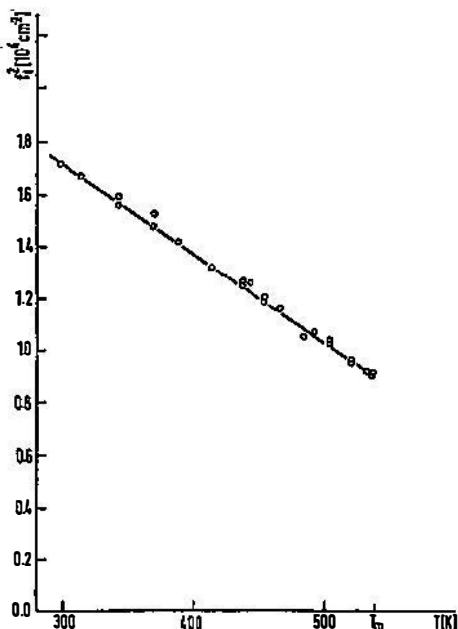


Fig. 4. Square of the chlorate ion's torsional frequency calculated from the  $\nu_4$  vs. temperature measurement.

this contribution is negligible. Another possibility is the anharmonicity of torsional vibrations at higher excitations. The estimated value for the average energy of a  $\text{ClO}_3^-$  ion, oscillating around  $x$  axis is  $3.9 \cdot 10^{-2}$  eV at 450 K, following from the harmonic oscillator approximation. The potential barrier for a rotation of the ion around the same axis was estimated in the reference<sup>5)</sup> to be 0.5 eV. It seems that the anharmonicity of torsional vibrations is likely to be important. In addition, one should not forget the interactions between the phonons<sup>11)</sup>. In the Raman spectra<sup>2,9)</sup> the linewidths of the phonons between  $72 \text{ cm}^{-1}$  and  $186 \text{ cm}^{-1}$  are of the same order of magnitude as the spacings among them. At high temperatures some of the lines become even superimposed to each other. So the modes which were at lower temperatures only translational might get some torsional components, which should be taken into account in the summation in Equ. (1) at high temperatures.

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## JEDRSKA KVADRUPOLNA REZONANCA KLORA IN VISOKOTEMPERATURNI FAZNI PREHOD V $\text{NaClO}_3$

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#### Vsebina

Ramanske in dielektrične meritve na kristalih  $\text{NaClO}_3$  nakazujejo možnost faznega prehoda iz ene trdne faze v drugo trdno fazo z ekstrapolirano temperaturo prehoda, ki je pri normalnem tlaku nad tališčem (537 K).

Z merjenjem jedrske kvadrupolne resonance  $^{35}\text{Cl}$  v odvisnosti od temperature in z uporabo Bayerjeve teorije smo lahko dobili temperaturni potek frekvenc torzijskih vibracij kloratnega iona. Primerjava z ramanskimi podatki kaže, da te frekvence ne ustrezajo domnevnomu kritičnemu nihanju (soft mode), ki se pojavlja pri ramanskih merjenjih.