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The Temperature Dependence of the Nuclear Quadrupole Resonance of ^{35}Cl in $KClO_3$, $AgClO_3$, $Ba(ClO_3)_2 \cdot H_2O$, and $Cu(ClO_3)_2 \cdot 6H_2O$

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The nuclear quadrupole resonance (NQR) frequencies of ^{35}Cl in $KClO_3$, $AgClO_3$, $Ba(ClO_3)_2 \cdot H_2O$, and $Cu(ClO_3)_2 \cdot 6H_2O$ have been measured as a function of the temperature in the range from 77 to 350 K at a constant (atmospheric) pressure. These data have then been analyzed by the method of Brown. The torsional frequencies of the ClO_3^- ion in the crystals have been determined by fitting the experimental data with the Bayer theory, modified by taking into account the anharmonicity in torsional oscillation. The low barrier height obtained in Cu salt indicates that a freer rotational motion of the chlorate ion is to be expected in this crystal.

Many attempts have been carried out to investigate the torsional oscillation in crystals through the NQR experiments. One approach is to determine the torsional frequency by measuring the temperature and the pressure dependences of the NQR frequencies by means of the theoreis developed by Bayer,[1] Kushida,[2] and Kushida, Benedek and Bloembergen.[3] Another approach is to study the characteristics of the torsional or reorientational motion by measuring the NQR line-width or the relaxation times as a function of the temperature.

The present investigation is of the former type. At lower temperatures, the Bayer theory (if there is a small torsional amplitude, so that the harmonic oscillation approximation is valid) gives a reliable torsional frequency in many cases, though not at very low temperatures. At higher temperatures, a large discrepancy appears between the theory and the experimental results. The purpose of the present work is to estimate the magnitude of the anharmonicity, using the quasi-harmonic approximation and assuning that the discrepancy originates from the anharmonic character of the torsional oscillation.

Experimental

The NQR signal was detected by means of a Kushida-type regenerative oscillator detector,[4] with a Zeeman modulation of an antisymmetric sinusoidal magnetic field of 30 Hz. The detected signals were suitably amplified by means of an audio-amplifier and automatically recorded on a chart (Hitachi Model QPD-33) through a lock-in-amplifier (NF Circuit Design Block Co., Model LI-572A). The resonance frequency was measured by means of pip marks at 1-kHz intervals on a chart which was generated by a frequency counter (Matsushita Communication Ind. Co., Model VP-0428). The details of the spectrometer system have been reported elsewhere.[5]

The accuracy in the frequency measurement is ± 0.1 kHz at the temperature of liquid nitrogen or at the freezing temperature of coolants, and is $\pm(0.2 \sim 0.1)$ kHz when the temperature is regulated by letting in cold nitrogen gas evaporated from the liquid-nitrogen container by heating it with a small heater. Combining with a chart-recorder voltmeter (Shimadzu Seisakusho, Ltd., Model A-521) for recording the junction voltage, a copper-constantan thermocouple was used to measure the temperature; it was affixed to the sample tube, which had been calibrated by the boiling temperatures of liquid nitrogen, benzene, and water,

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[1] H. Bayer, *Z. Physik*, **130**, 227 (1951).

[2] T. Kushida, *J. Sci. Hiroshima Univ. Ser. A*, **19**, 327 (1955).

[3] T. Kushida, G. B. Benedek, and N. Bloembergen, *Phys. Rev.*, **104**, 1364 (1956).

[4] T. Cole, T. Kushida and H. C. Heller, *J. Chem. Phys.*, **38**, 2915 (1963).

[5] M. Suhara, *Sci. Rep. Kanazawa Univ.*, **17**, 7 (1972).

the sublimation temperature of dry ice, and the triple point of water. The error in the temperature measurement was ±0.5 K, which causes an ambiguity in the resonance frequency of ±1 kHz.

The calculation of the best-fitting parameters in the theoretical equation was carried out by using a digital computer, FACOM 230-35, at Kanazawa University. The errors in the calculated parameters were estimated by assuming the condence coefficient to be 0.99.

The $AgClO_3$ was prepared by mixing hot aqueous solutions of 0.5 M of $AgNO_3$ and 0.5 M of $NaClO_3$, cooling the mixture in a refrigerator, filtering the crystals, and repeating the recrystallization. The sample must be kept in the dark. The $KClO_3$ and $Ba(ClO_3)_2 \cdot H_2O$ were commericial grade materials purified by repeating the recrystallization from hot water. The $Cu(ClO_3)_2 \cdot 6H_2O$ was obtained by mixing a hot aqueous solution of 1 M of $CuSO_4 \cdot 5H_2O$ and $Ba(ClO_3)_2 \cdot H_2O$, filtering off the $BaSO_4$ by means of No. 50 filterpaper, evaporating the blue filtrate at room temperature by a vacuum pump, filtering the crystals, and then repeating the recrystallization from cold water.

Results and Discussion

The NQR of ^{35}Cl in K, Ag, Ba, and Cu chlorates has been detected from 77 K to 350 K. The observed spectrum of each chlorates consists of a single line. This fact indicates that all the chlorate ions in a unit cell are located in crystallographically-equivalent positions; this could be expected from the crystal structure except for the Cu salt, whose structure has not been known. The resonances of the K and Ag salts were rather more intense than others throughout the temperature region examined.

The temperature dependence of the resonance frequency is shown in Fig. 1, together with the results of the previous works. The resonance frequencies of these four chlorates at the temperature of liquid nitrogen were in good agreement with the reported data, but at room temperature there was a large discrepancy between Moshier's results[6] and the present ones except in the case of K salt. When the temperature variation was repeated (by increasing or decreasing it), the temperature dependence showed a good reproducibility, so the phase transitions have not been detected in all the chlorates. The intensity of each line decreased with an increase in the temperature.

The experimental data were analyzed by the method of Brown,[7] in which the temperature dependence of the resonance frequency is represented by a polynomial of the form:

$$\nu(T) = a_0 + a_1 T + a_2 T^2 \qquad (1)$$

where:

$$a_0 = \nu_0$$

$$a_1 = -3ka_0/(4\pi^2 \nu_{t0}{}^2 \Theta)$$

$$a_2 = 2a_1 g$$

$\nu(T)$ and ν_0 are the NQR frequencies at T and 0 K respectively, Θ is a constant moment of inertia, and ν_{t0}, a torsional oscillation frequency. In this analysis, a quasi-harmonic approximation for the anharmonic oscillation is used; the temperature variation in the torsional frequency is assumed to be:[8]

$$\nu_t = \nu_{t0}(1 - gT) \qquad (2)$$

with g a small positive constant. From the experimentally-determined values of a_0, a_1, and a_2, the values of ν_{t0} and g have been evaluated, using 83×10^{-40} g·cm^2 as the value of Θ. The results are summarized in Table 1. together with the values for Ca salt obtained by Kumar and Nageswara Rao.[9] The uncertainties in the g and ν_t values were $\pm 0.2 \times 10^{-4}$ K^{-1} and ±2 cm^{-1} respectively. The a_1 values for the four chlorates are of the same order of magnitude, but the a_2 values for Ag and Ba salts are rather smaller than those of the others. On the other hand, the a_1 value in Ca salt is significantly smaller than those of the four chlorates, although the a_2 values lie in the middle between them. Since the values of a_0 in all the chlorates considered are 29~30 MHz, the difference in the coefficient, a_1, indicates the difference in the torsional frequency at 0 K, when all the chlorate ions have the same value of the moment of inertia. The torsional frequencies at 0 K and 300 K are also shown in Table 1.

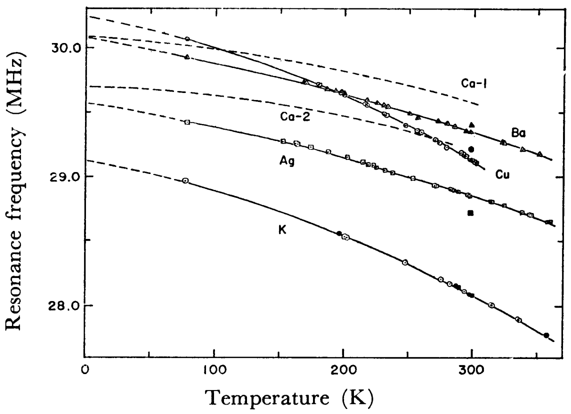

Fig. 1. Temperature dependence of the NQR frequencies of ^{35}Cl in several chlorates.

The quoted data are indicated by the corresponding solid symbols except Ca salt, for which the broken lines are used.

Chlorates	Literatures
K	a, b, c, d, e
Ag	f
Ba	f, g
Cu	f, h
Ca	i

a) T. C. Wang, C. H. Townes, A. L. Schawlow, and A. N. Holden, *Phys. Rev.*, **86**, 809 (1952).
b) H. Zeldes and H. Livingston, *J. Chem. Phys.*, **26**, 1102 (1957).
c) Ref. (3) in text.
d) N. Negita and S. Saton, This Bulletin, **29**, 426 (1956).
e) P. J. Bray and R. G. Barnes, *J. Chem. Phys.*, **22**, 2023 (1954).
f) Ref. (6) in text.
g) P. J. Bray and P. J. Ring., *J. Chem. Phys.*, **21**, 2226 (1953).
h) P. J. Bray, *ibid.*, **23**, 703 (1955).
i) Ref. (9) in text.

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[6] R. W. Moshier, *Inorg. Chem.*, **3**, 199 (1964).

[7] R. J. Brown, *J. Chem. Phys.*, **32**, 116 (1960).

[8] I. Ichishima, *Nippon Kagaku Zassi*, **71**, 607 (1950)., A. A. Maradudin and R. F. Wallace, *Phys. Rev.*, **125**, 1277 (1962).

[9] U. V. Kumar and B. D. Nageswara Rao, *Phys. Stat. Solid.*, **B44**, 203 (1971).

TABLE 1. VALUES OF THE FITTING PARAMETERS; a_0, a_1 AND a_2, AND CALCULATED VALUES; $\langle g \rangle$, ν_t AND V_0.

		$KClO_3$	$AgClO_3$	$Ba(ClO_3)_2\cdot H_2O$	$Cu(ClO_3)_2\cdot 6H_2O$	$Ca(ClO_3)_2\cdot 2H_2O$[a)	
						ν_1	ν_2
a_0 (kHz)		29131.9 ±1.6	29576.6 ±4.0	30080.9 ±3.4	30241.5 ±3.2	30087.6 ±1.2	29699.5 ±1.3
a_1 (kHz/K)		−1.861 ±0.007	−1.584 ±0.015	−1.719 ±0.013	−1.768 ±0.013	−0.665 ±0.013	−0.211 ±0.015
a_2 (10^{-3} kHz/K^2)		−5.48 ±0.03	−2.80 ±0.05	−2.51 ±0.04	−6.51 ±0.05	−3.41 ±0.03	−4.67 ±0.04
$\langle g \rangle$ (10^{-4} K^{-1})		14.7	8.8	7.3	18.4	25.64	110.7
ν_t (cm^{-1})	0 K	148	162	156	155	178	325
	300 K	81	114	122	70	44[b)	—
V_0 (kcal/mol)	77 K	140	185	178	143	164[b)	19[b)
	300 K	56	106	122	39	15[b)	—

a) Ref. 9 in text.
b) Calculated from the results of Ref. 9 in text.

Using different assumptions and methods, the temperature dependence of the resonance frequency of ^{35}Cl in $KClO_3$ has been analyzed in various temperature regions by three authors.[3,10,12) The torsional frequency thus obtained has been compared with the room-temperature values[11) of the Raman lines; 54, 82, 98, 127, and 145 cm^{-1}.

From the present analysis, which differs from the above three the torsional frequency at room temperature, was found to be $\nu_t(300)=81$ cm^{-1}, which was in agreement with the observed Raman line[11) at 82 cm^{-1} at 297 K. The g value was found to be 1.47×10^{-3} K^{-1}, which was larger than the 2×10^{-4} K^{-1} for the 98 cm^{-1} line; the temperature coefficient for the 82 cm^{-1} line has not been measured, however.

Recently, the temperature dependence of the resonance frequency in $Ba(ClO_3)_2\cdot H_2O$ has been independently measured by Ramanohan and Sobhanadri.[13) The same procedure as that in the present study has been employed to analyze the experimental data. The parameters obtained by them give the values of 30039.7 kHz, −1.45 kHz/K, and -3.28×10^{-3} kHz/K^2 for a_0, a_1, and a_2 respectively; these values are in agreement with the present results. The torsional frequency of 125 cm^{-1} at 300 K is also in good agreement with the present finding.

If a simple sinusoidal potential for the torsional oscillation in crystal is assumed, the frequency, ν_t, is given by:[14)

$$\nu_t = (n/2\pi)\sqrt{V_0/(2\Theta)} \qquad (3)$$

where V_0 is the height of the potential barrier with an n-th-fold symmetry. In Table 1, the calculated V_0 values are shown. The potential barrier substantially decreases with an increase in the temperature. This indicates that the chlorate ion may rotate at the crystal site at room temperature; then the torsional oscillation has a large amplitude, so anharmonic motion takes place. In Ag and Ba salts it can be seen that the torsional motion of the chlorate ion as a whole hardly occurs, even at room temperature. On the other hand, a freer rotational motion can be expected in Ca and Cu salts from the low barrier height, which is of nearly the same order as, or several times larger in magnitude than that in organic molecular crystals—*i.e.*, it is of the order of 10 kcal/mole.[15) In Ca salt, it is clear from the results reported by Kumar *et al.*[9) that ν_2 has an anomalous temperature dependence. A very large g value gives a negative $(1-gT)$ factor at room temperature. Although Kumar *et al.* did not discuss this fact, it can be suggested that the present method for the analysis of the experimental results can not be used to illustrate the motion of the chlorate ion in the crystal site corresponding to ν_2.

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11) C. S. Kumari, *Proc. Indian Acad. Sci.*, **23A** 177 (1950).
12) D. B. Utton, *J. Chem. Phys.*, **47**, 371 (1967).
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14) G. Herzberg, "Molecular Spectra and Molecular Structure", II, D. Van Nostrand, New York (1949), p. 226.
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