THERMAL EXPANSION OF SODIUM CHLORATE AND BROMATE

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Abstract

The thermal expansion of sodium chlorate has been measured from −151.3°C to +11.4°C and is found to join up well with the high temperature data of Sharma (1950).

The expansion coefficient of sodium bromate was investigated from −149°C to +171.5°C. The high temperature data are not in agreement with Sharma's values.

Using an approximate vibration spectrum which corresponds roughly with the observed Raman effect data, the specific heat and thermal expansion of sodium chlorate can be satisfactorily accounted for. The empirically chosen Grüneisen constants for the internal and lattice oscillations to account for the thermal expansion correspond closely to the values determined from the temperature variation of Raman spectrum for this crystal.

Introduction

An exhasutive study of the Raman spectrum of sodium chlorate has been carried out by different investigators (Rousset, Laval and Lochet, 1943; Shantakumari, 1948, 1950; Chandrasekharan, 1950). The specific heat of this crystal has also been measured from −191°C to 255°C (Ewald, 1914; Goodwin and Kalmus, 1909). Sharma (1950) has determined the thermal expansion of this crystal from room temperature to 226°C. So it appeared worthwhile to extend the expansion measurements to liquid air temperature and to account for the specific heat and thermal expansion of this crystal on an approximate vibration spectrum which conforms roughly to the observed Raman effect data.

At the same time, the thermal expansion of sodium bromate also was studied from −149°C to 171°C. The expansion of this crystal has been studied above room temperature by Mason (1946) and Sharma (1950) but there appears to be some discrepancy in their measurements.

Experimental Details and Results

The thermal expansion of these crystals have been studied with the interferometric technique in use here (Press, 1949; Sridhar, 1952). The temperature was measured with a chromel alumel thermocouple in conjunction with a Pye precision Vernier potentiometer reading upto ± 1 μv. The precautions mentioned by White (1941) for leakage prevention were followed.

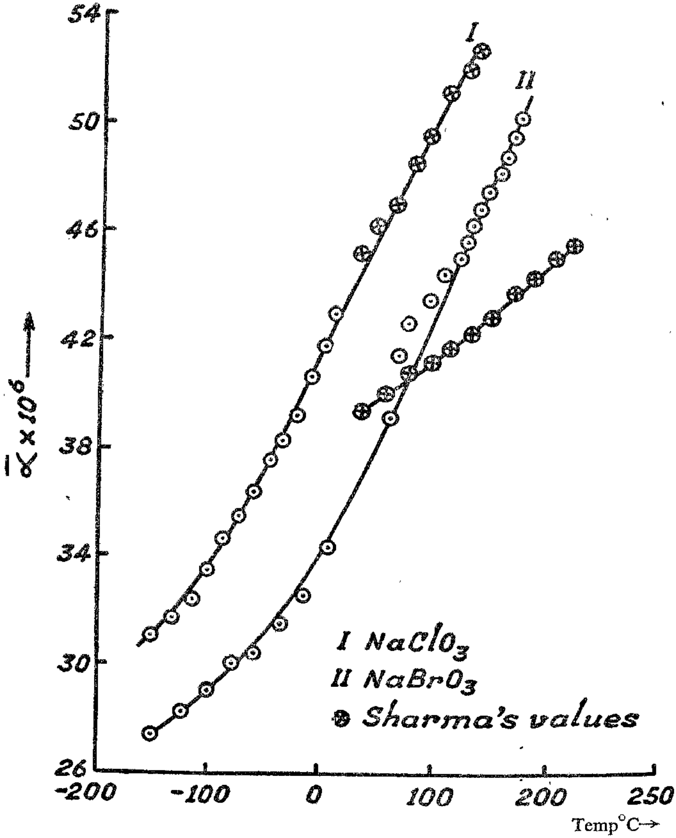

FIG I

$\bar{\alpha}$ Vs T curve of $NaClO_3$ and $NaBrO_3$

The crystals were solution grown in this laboratory by Mr. C. P. Gopalakrishnan, to whom the author's thanks are due. Pyramids of 0.459 cm. height were prepared from this sodium chlorate crystal. In the case of sodium bromate two sets of pyramids of heights 0.493 cm. and 0.418 cm. were used. The measurements were repeated two or three times.

In the following tables are given the values $\bar{\alpha}$ of the linear expansion coefficient of sodium chlorate and sodium bromate. The expansion coefficient $\bar{\alpha}$ is plotted as a function of temperature in Fig. I.

TABLE I

Linear expansion coefficient of $NaClO_3$

Temperature °C	$\bar{\alpha} \times 10^6$	Temperature	$\bar{\alpha} \times 10^6$
− 151.3	30.98	− 48.4	37.42
− 133.5	31.64	− 35.2	38.15
− 117.6	32.33	− 22.2	39.14
− 103.2	33.43	− 10.4	40.48
− 89.4	34.59	+ 1.3	41.61
− 75.42	35.42	+ 11.4	42.81
− 61.8	36.28	....	....

Linear expansion coefficient of $NaBrO_3$

Temperature	$\bar{\alpha} \times 10^6$	Temperature	$\bar{\alpha} \times 10^6$
− 149.0	27.43	53.2	37.74
− 125.8	28.26	67.7	41.54
− 102.0	29.16	81.4	43.10
− 79.5	30.11	94.3	43.38
− 58.0	30.77	106.5	44.23
− 36.8	31.48	119.2	44.81
− 15.4	32.59	131.3	46.02
+ 4.1	34.60	143.0	47.30
....	....	154.8	47.96
....	....	160.4	48.65
....	....	171.5	50.08

From Fig. I it is apparent that the present data for sodium chlorate between − 151.3°C and + 11.4°C joins up well with Sharma's values above room temperature. This is not so in the case of sodium bromate. Repeated measurements on different specimens gave concordant results which were in disagreement with the values in the literature. The reason for this discrepancy is not known.

DISCUSSION

Sodium chlorate belongs to the class T of the cubic system and possesses 4 molecules per unit cell. The 60 degrees of freedom of the unit cell can be apportioned among the internal oscillations, lattice oscillations and translations as per the following table (Couture and Mathieu. 1948).

TABLE II

Internal oscillations	... 2 (A), 2 (E), 6 (F)
Lattice oscillations	
1. Librations	... 1 (A), 1 (E), 3 (F)
2. Translatory oscillations	... 2 (A), 2 (E), 5 (F)
Pure Translations	... 3

Total number of modes of vibrations of the unit cell = 60.

From the Raman effect data Shantakumari (1948) has classified the observed frequencies as follows:

Internal Oscillations :—

Internal Oscillations:	482 (E), 487 (F), 627 (F), 933 (F), 936 (A), 959 (E), 966 (F), 984 (F), 1028 (?).
Latttice Oscillations:	70 (E), 83 (F), 103 (F), 122.7 (F), 131 (A), 179 (E).

We see that the internal oscillations fall into two groups—those whose frequencies lie between 900 to 1100 cm^{-1} and those whose frequencies lie between 400 to 600 cm^{-1}. We approximate the frequencies belonging to each one of these groups by a single frequency which will be some sort of an average of the frequencies belonging to the group. So writing ν_1 to represent the frequency belonging to group 1 of the internal oscillations, ν_2 the frequency of group 2 of the internal oscillations, ν_L the frequency of the lattice oscillations and ν_D the Debye frequency to represent the translations we can write the expression for the specific heat as

$$C_v = \tfrac{1}{12}\{15H(\theta_1/T) + 9H(\theta_2/T) + 33H(\theta_L/T) + 3C(\theta_D/T)\}$$

where
$$H(x) = \frac{3R\, e^{x} x^{2}}{(e^{x}-1)^{2}}$$

and
$$C(x) = 3R\frac{12}{x^{3}}\int_{0}^{x} \frac{\zeta^{3}}{e^{\zeta}-1}\, d\zeta - \frac{3x}{e^{x}-1}$$

The values of θ_1, θ_2 & θ_L have been chosen to give good agreement with the experimental results while θ_D has been calculated using the elastic constants of Mason (1946).

The values of θ_1, θ_2, θ_L and θ_D come out to be

$$\begin{aligned} \theta_1 &= 1400^\circ\mathrm{K} \\ \theta_2 &= 600^\circ\mathrm{K} \\ \theta_L &= 180^\circ\mathrm{K} \\ \theta_D &= 133^\circ\mathrm{K} \end{aligned}$$

In the following table the specific heat calculated from the approximate vibration spectrum is compared with the observed value.

TABLE III

Temperature	C_v calculated	C_v experimental
192°K	15.71	15.7
273°K	20.84	20.8
301°K	22.89	22.5
380°K	24.65	24.5
406°K	25.1	25.7

Using this vibration spectrum the expansion coefficient can be calculated using the formula

$$B = 3\alpha = (\chi_0/V_0)\cdot\tfrac{1}{12}\times$$
$$\times\frac{15\gamma_1 H(\theta_1/T) + 9\gamma_2 H(\theta_2/T) + 33\gamma_L H(\theta_L/T) + 3\gamma_D C(\theta_D/T)}{\{1-(k\chi_0/V_0)\tfrac{1}{12}[15\gamma_1 E(\theta_1/T) + 9\gamma_2 E(\theta_2/T) + 33\gamma_L E(\theta_L/T) + 3\gamma_D D(\theta_D/T)]\}^{2}}$$

where χ_0 = compressibility = $3.88\times10^{-12}\ \mathrm{cm}^2/\mathrm{dyne}$.
V_0 = Molar volume = M/ρ = 42.74 cc.
$\gamma_i = -d\log\nu_i/d\log\nu$ = Grüneisen constant for the frequency ν_i
k = an arbitrary constant.

Here
$$E(x) = 3RT\frac{x}{e^{x}-1}$$

and

$$D(x) = 3RT\frac{3}{x^3}\int_0^x \frac{\xi^3}{e^{\xi} - 1}\, d\xi$$

Choosing $\gamma_1 = 0.1$; $\gamma_2 = 0.2$; $\gamma_L = 1.44$; $\gamma_D = 1.9$; and $k = 5.5$ it is possible to account for the experimental variation of $\bar{\alpha}$ *versus* T in a satisfactory manner. In the following table the calculated and experimentally observed values of α are given.

TABLE IV

Temp. k	$\beta = 3\bar{\alpha}$ (Vol. expn. cocff.) expl.	$\beta = 3\bar{\alpha}$ Cal.	Temp.	$\beta = 3\bar{\alpha}$ (Vol. expn. coeff.) expl.	$\beta = 3\bar{\alpha}$ Cal.
121.67	91.23	91.23	338.5	140.43	139.89
155.36	99.6	101.10	368.2	147.78	146.4
183.63	103.77	103.44	396.3	154.98	153.00
211.21	110.98	113.1	423.5	160.56	159.3
237.00	114.45	119.5	449.7	165.39	165.9
262.00	121.24	124.2	474.8	173.37	172.59
284.4	128.43	128.6	498.9	179.07	179.19
307.2	134.76	133.38	.....	..	—

From a study of the temperature variation of Raman spectrum (Shantakumari, 1950) the γ values for the various frequencies can be calculated. For the internal oscillation γ is of the order of 0.1 and for the lattice oscillations γ is of the order of 1.4. These values correspond closely to the values of γ chosen empirically to account for the expansion of this crystal.

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