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Elastic, Piezoelectric, and Dielectric Properties of Sodium Chlorate and Sodium Bromate

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The elastic, piezoelectric, and dielectric constants of sodium chlorate ($NaClO_3$) and sodium bromate ($NaBrO_3$) have been measured over a wide temperature range. The value of the piezoelectric constant at room temperature is somewhat larger than that found by Pockels. The value of the Poisson's ratio was found to be positive and equal to 0.23 in contrast to Voigt's measured value of -0.51. At high temperatures the dielectric and piezoelectric constants increase and indicate the presence of a transformation point which occurs at a temperature slightly larger than the melting point. A large dipole piezoelectric constant (ratio of lattice distortion to dipole polarization) results for these crystals but the electromechanical coupling factor is small because the dipole polarization is small compared to the electronic and ionic polarization and little of the applied electrical energy goes into orienting the dipoles.

I. INTRODUCTION

SODIUM chlorate ($NaClO_3$) is a water soluble crystal which crystallizes in the cubic tetrahedral class. As a consequence of its symmetry, it has three elastic constants, one piezoelectric constant, and one dielectric constant. Its isomorphous salt, sodium bromate ($NaBrO_3$), crystallizes in the same crystal class. Measurements were made of the piezoelectric constant of sodium chlorate as early as 1893 by Pockels[1] who obtained a value of 4.84×10^{-8} for the piezoelectric constant d_{14}. Voigt[2] measured the elastic constants and came to the conclusion that the crystal had a negative Poisson's ratio; i.e., the crystal expands sidewise as it elongates lengthwise. The measurements made here do not confirm this conclusion. Since this crystal has such a simple structure, has no water of crystallization, and will stand a high temperature (up to 250°C), it was thought worth while to investigate its properties even though the indicated piezoelectric effect was quite small.

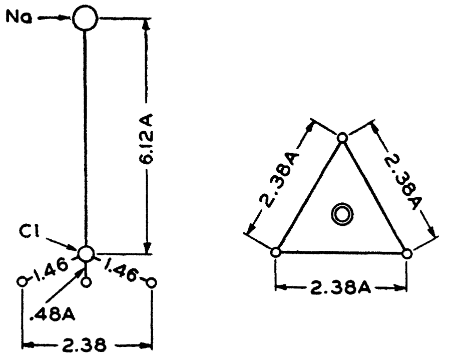

FIG. 1. Arrangement of atoms in sodium chlorate molecule.

X-ray crystal structure studies[3] show that sodium chlorate has four molecules per unit cell. Each molecule consists of three oxygens arranged in the form of an equilateral triangle with a separation of 2.38A between oxygen centers as shown by Fig. 1. The chlorine is located at a distance of 0.48A above the plane of the oxygen atoms in a line through the center of gravity of the oxygens. The sodium lies above the chlorine at a distance of 6.12A. On account of the large separation of the sodium from the chlorate ion, it is probably the latter which acts as the dipole in

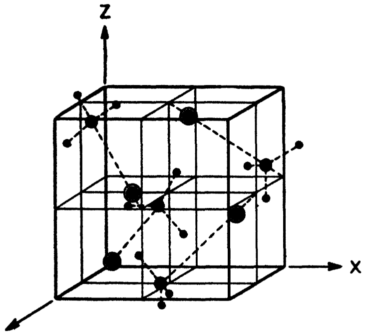

FIG. 2. Arrangement of sodium chlorate molecules in unit crystal cell.

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[1] W. Voigt, *Lehrbuch Der Kristall Physik*, p. 873.

[2] W. Voigt, *Lehrbuch Der Kristall Physik*, p. 741.

[3] R. W. G. Wyckoff, *The Structure of Crystals* (Chemical Catalog Company, New York), p. 276.

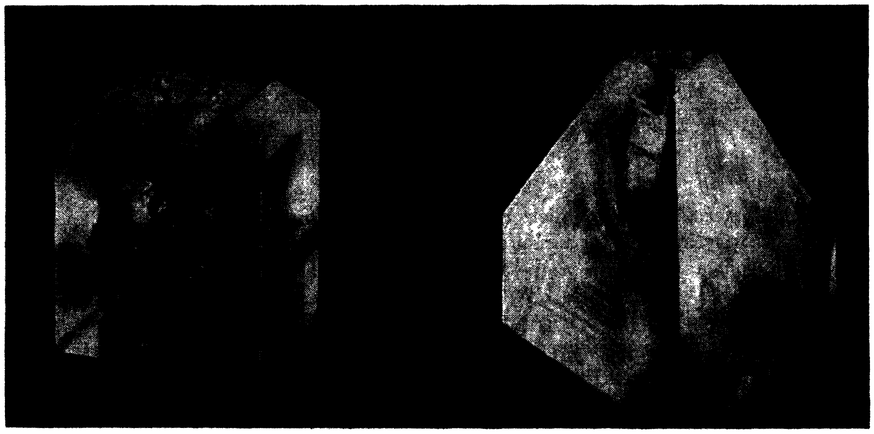

FIG. 3. Photograph of sodium chlorate crystal (left) and sodium bromate crystal (right).

the temperature variable part of the dielectric constant. The arrangement of the four molecules in the unit cell is shown by Fig. 2.

The experimental results for the dielectric constant show that there is a component of the polarization which is practically independent of the temperature and another component which increases with temperature and becomes large as the melting point is approached. This is presumably caused either by an actual orientation of the chlorate dipoles as they become unfrozen at the higher temperature, or caused by an apex reversal of the position of the chlorine in the molecule. The fact that the Curie temperature is only slightly above the melting temperature points rather strongly to the first alternative since there is no reason to expect that an apex reversal would be connected with the melting of the crystal. The piezoelectric measurements show that the piezoelectric stress due to an applied field is directly proportional to the temperature variable component of the polarization and hence it is the change in orientation of the dipoles which causes the distortion of the crystal lattice and hence the piezoelectric effect.

Similar measurements have been made for the isomorphous salt sodium bromate. The temperature independent dielectric constant is larger than for sodium chlorate, indicating that the polarizability of the bromine is larger than that for the chlorine. For equal temperature separations from the Curie point (which is close to the melting point) the temperature variable portion of the polarization is nearly the same size as that for sodium chlorate, indicating that the effective dipole moment is nearly the same. The piezoelectric measurements show that a given dipole polarization produces over twice the lattice distortion and hence piezoelectric effect for sodium bromate as for sodium chlorate.

II. SYMMETRY CONSIDERATIONS AND THE RESULTING PIEZOELECTRIC EQUATIONS

Crystals of sodium chlorate and sodium bromate have been grown by A. N. Holden from a saturated water solution by slowly reducing the temperature and depositing the salt on a prepared seed. The process will be described in a forthcoming paper. Both crystals belong to the cubic tetrahedral class but there is an interesting difference in their crystal habits. Figure 3 shows a photograph of a sodium chlorate and a sodium bromate crystal. The chlorate crystal assumes a cubic form of which the principal faces are the 001, 010, and 100 planes. On the cube edges the 110, 101, and 011 planes are sometimes in evidence. For the bromate crystal, on the other hand, the habit is the tetragonal one. The principal planes are the 111 planes.

Because of the symmetry of the crystal, there are three elastic constants, one piezoelectric constant, and one dielectric constant. For the purpose of this paper it is advantageous to express the piezoelectric relations in the form of a ratio of the strain to the electric displacement. This follows from the fact that it is found that the strain is nearly proportional to the temperature variable part of the polarization. Since a system of equations, which involves quantities that can be directly measured, cannot be based on the polarization or a part of the polarization, the electrical displacement is employed. As will be shown, the polarization constants are easily obtained from these and the measured dielectric constants.

On this basis the piezoelectric equations for sodium chlorate or sodium bromate can be written

$$\begin{aligned}
S_1&=s_{11}T_1+s_{12}T_2+s_{12}T_3, & S_6&=s_{44}{}^DT_6+g_{14}\frac{D_z}{4\pi},\\
S_2&=s_{12}T_1+s_{11}T_2+s_{12}T_3, & E_x&=\frac{D_x}{\epsilon_1{}^T}-g_{14}T_4,\\
S_3&=s_{12}T_1+s_{12}T_2+s_{11}T_3, & E_y&=\frac{D_y}{\epsilon_1{}^T}-g_{14}T_5,\\
S_4&=s_{44}{}^DT_4+g_{14}\frac{D_x}{4\pi}, & E_z&=\frac{D_z}{\epsilon_1{}^T}-g_{14}T_6,\\
S_5&=s_{44}{}^DT_5+g_{14}\frac{D_y}{4\pi},
\end{aligned}\tag{1}$$

where $S_1, \cdots, S_6$ are the six strain components, $T_1, \cdots, T_6$ the six stress components, $E_x, \cdots, E_z$ the three field strengths in the three directions, $D_x, \cdots, D_z$ the three electric displacements which at the surface are equal to the surface charges times 4π, s_{11}, s_{12}, $s_{44}{}^D$ the three elastic constants, g_{14} the piezoelectric constant which measures the ratio of the strain to the surface charge in the absence of a stress, and $\epsilon_1{}^T$ the dielectric constant, that is the same in every direction. The elastic constant $s_{44}{}^D$ has a superscript D to show that it is the ratio of the strain to the applied stress when the electric displacement is constant or zero. Similarly the dielectric constant $\epsilon_1{}^T$ has a superscript T to indicate that it is the "free" dielectric constant measured in the absence of an applied stress.

Another form of the piezoelectric equations in which the stresses are expressed as a function of the strain is also of interest. These can be obtained from Eqs. (1) by solving for the stresses in terms of the strains. These become

$$\begin{aligned}
T_1&=c_{11}S_1+c_{12}S_2+c_{12}S_3, & T_6&=c_{44}{}^DS_6-h_{14}\frac{D_z}{4\pi},\\
T_2&=c_{12}S_1+c_{11}S_2+c_{12}S_3, & E_x&=\frac{D_x}{\epsilon_1{}^S}-h_{14}S_4,\\
T_3&=c_{12}S_1+c_{12}S_2+c_{11}S_3, & E_y&=\frac{D_y}{\epsilon_1{}^S}-h_{14}S_5,\\
T_4&=c_{44}{}^DS_4-h_{14}\frac{D_x}{4\pi}, & E_z&=\frac{D_z}{\epsilon_1{}^S}-h_{14}S_6,\\
T_5&=c_{44}{}^DS_5-h_{14}\frac{D_y}{4\pi},
\end{aligned}\tag{2}$$

where

$$\begin{aligned}
c_{11}&=\frac{s_{11}+s_{12}}{s_{11}(s_{11}+s_{12})-2s_{12}{}^2},\\
c_{12}&=\frac{-s_{12}}{s_{11}(s_{11}+s_{12})-2s_{12}{}^2},\\
c_{44}{}^D&=\frac{1}{s_{44}{}^D},\quad h_{14}=g_{14}c_{44}{}^D,\\
\frac{4\pi}{\epsilon_1{}^S}&=\frac{4\pi}{\epsilon_1{}^T}+g_{14}h_{14}=\frac{4\pi}{\epsilon_1{}^T}+\frac{g_{14}{}^2}{s_{44}{}^D}.
\end{aligned}\tag{3}$$

Here $\epsilon_1{}^S$ denotes the "clamped" dielectric constant, i.e., the dielectric constant measured in the absence of a strain. It is related to the "free" dielectric constant as indicated in Eq. (3).

If we wish to test whether the piezoelectric strain is caused by the temperature variable part of the polarization, we can write

$$\begin{aligned}
\frac{D_x}{4\pi}&=\sigma_x=\frac{E_x}{4\pi}+P_{x0}+P_x{}'\\
&=\frac{E_x}{4\pi}[1+4\pi\eta_0]+P_x{}'=\frac{E_x\epsilon_0}{4\pi}+P_x{}',
\end{aligned}\tag{4}$$

where ϵ_0 is the temperature and strain independent part of the dielectric constant. Introducing this value into Eq. (2) and eliminating common terms, the equations involving the piezoelectric effect become

$$T_4 = c_{44}{}^{*} S_4 - f_{14} P_x{}', \quad E_x = \frac{4\pi P_x{}'}{\epsilon_1{}^S - \epsilon_0} - f_{14} S_4,$$

where (5)

$$f_{14} = \frac{h_{14}\epsilon_1{}^S}{\epsilon_1{}^S - \epsilon_0}, \quad c_{44}{}^{*} = c_{44}{}^D + \frac{h_{14}{}^2 \epsilon_0 \epsilon_1{}^S}{4\pi(\epsilon_1{}^S - \epsilon_0)}$$

$c_{44}{}^{*}$ is the elastic compliance with $P_x{}'$ held constant or zero. f_{14} is the ratio of the stress to the temperature variable part of the polarization in the absence of an internal strain. Hence if the piezoelectric constant g_{14} or h_{14} and the constant and temperature variable parts of the dielectric constant are determined, the ratio of stress to temperature variable polarization can be evaluated.

The method of evaluating the piezoelectric constant employed has been to utilize a longitudinally vibrating crystal cut with its length at 45° from two of the axes and with its thickness along the third axis. The measurements made are an evaluation of the capacity at low frequencies (free dielectric constant) and the resonant and anti-resonant frequencies. Since the relation between these quantities has been discussed at length in another publication,[4] only the pertinent equations will be given here.

The frequency of resonance of the longitudinally vibrating plated crystal and the measured density determine the elastic compliance at constant field according to the equation

$$s^E = \frac{1}{(2lf_R)^2 \rho}, \tag{6}$$

where l is the length of the crystal, f_R the resonant frequency, and ρ the density. The separation Δf between resonant and antiresonant frequencies, determines the electromechanical coupling constant k, according to the formula

$$k = \frac{1}{\left(1 + \frac{4}{\pi^2}\frac{f_R}{\Delta f}\right)^{\frac{1}{2}}}, \tag{7}$$

where k the coupling factor is defined in terms of the fundamental constants by the equation

$$k = g\left(\frac{\epsilon^T}{4\pi s^E}\right)^{\frac{1}{2}}. \tag{8}$$

In this equation g is the longitudinal piezoelectric constant relating the strain to the applied charge, ϵ^T the free dielectric constant normal to the

Table I. Measured properties of sodium chlorate.

Temperature in degrees C	Z-cut; L = 22.5° from X L = 20.13 mm W = 2.69 mm T = 1.00 mm	Z-cut; L = 45° from X L = 20.38 mm W = 2.71 mm T = 1.01 mm	0° Z-cut L = 29.90 mm W = 6.02 mm T = 1.04 mm	$\Delta f/f_R$ for 45° Z-cut	Free dielectric constant $\epsilon_1{}^T$
28	193.2 kc cm	181.8 kc cm	108.6	0.000281	5.76
40	192.2	180.9	108.3	0.000317	5.8
75	190.2	179.3	108.2	0.000393	5.94
100	187.2	177.2	106.2	0.000465	6.05
130	183.4	173.5	104.2	0.000584	6.21
140	182.3	172.5	103.8	0.00065	6.27
150	181.3	171.3	103.1	0.000725	6.34
160	—	170.3	102.5	0.000807	6.41
170	178.6	169.2	102.0	0.000894	6.49
180	177.5	168.3	101.2	0.00098	6.57
190	176.1	167.1	100.4	0.00115	6.70
200	175.1	166.2	99.9	0.00134	6.81
210	173.1	164.5	99.1		
220	172.2	163.3	98.3		
230	170.3	161.3	97.2		
240	168.5	160.2	96.2		

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[4] See W. P. Mason, Phys. Rev. 69, 173–195 (1946).

SUBSTANCE	COEF. OF THERMAL EXPANSION ($10^6 \times \Delta l/l$ PER DEGREE C)			$\Delta l/l = a(t-25) + b(t-25)^2$	
	-40° TO 0°	0° TO 50°	50° TO 90°	$10^5 \times a$	$10^8 \times b$
S.B.	37.5	39.2	41.7	3.94	1.0
S.C.	40.8	43.4	45.2	4.36	3.6

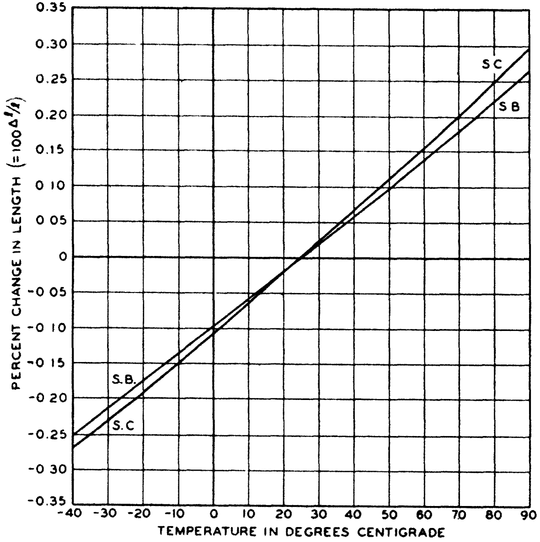

FIG. 4. Percent linear thermal expansion of sodium bromate and sodium chlorate.

applied voltage, and s^E the inverse of Young's modulus along the length of the crystal measured at constant field.

Measurements with longitudinally vibrating crystals will determine one elastic constant and a relation between the other two. To determine the shear elastic constant requires a measurement of a shear vibrating crystal. It has been shown previously[4] that a face shear mode of a long thin crystal will determine the shear elastic constant according to the equation

$$s^E = \frac{1}{(2l_w f_R)^2 \rho}, \tag{9}$$

where l_w is the width of the shear vibrating crystal. The coupling for a shear mode is determined by Eq. (7) if the coupling is defined as in Eq. (8) using the shear piezoelectric constant and the shear elastic constant.

III. MEASUREMENT OF PRIMARY ELASTIC, PIEZOELECTRIC, AND DIELECTRIC CONSTANTS OF SODIUM CHLORATE AND SODIUM BROMATE

All of the constants of these crystals can be measured by measuring the properties of three oriented cuts. All cuts are taken normal to one of the crystallographic axes, which for convenience will be designated the Z axis. One cut has its length 45° from the other two axes, one cut has its length 22.5° from one of the axes, and the third cut has its length along one of the crystallographic axes. The first two cuts are driven in their lowest longitudinal mode and are made long compared to their width or thickness so that the uncorrected compliance constant $s_{11}^{E'}$ is determined. As a function of orientation this compliance is given by the equation.

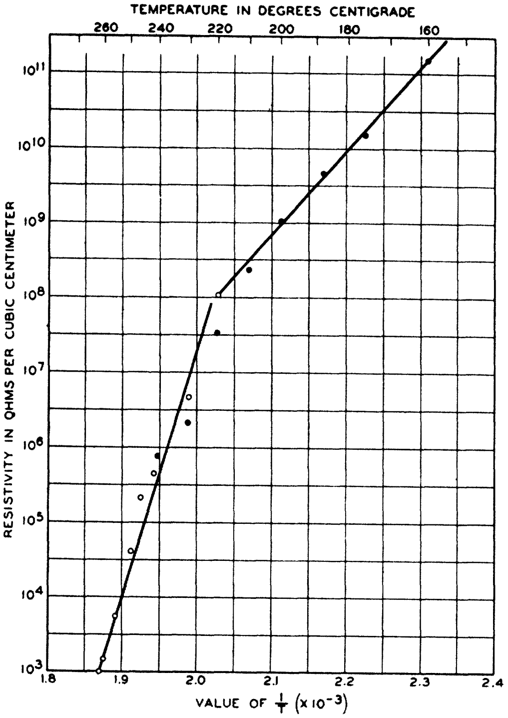

FIG. 5. Resistivity as a function of temperature.

$$s_{11}^{E'} = s_{11}(\cos^4 \varphi + \sin^4 \varphi) + (2s_{12} + s_{44}^E) \sin^2 \varphi \cos^2 \varphi. \tag{10}$$

Hence measurements of the resonant frequencies, the expansion coefficient of the material, and the density at 25°C will determine two values of $s_{11}^{E'}$ for two different angles and hence s_{11} and $(2s_{12} + s_{44}^E)$ can be evaluated over a range of temperatures. The third crystal is cut thin, and with its width dimension much smaller than its length. It was demonstrated in a previous paper[4] that the resonant frequency of the face shear

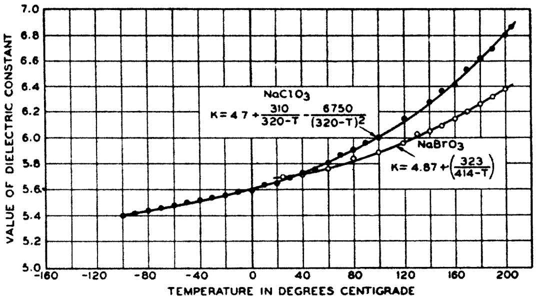

FIG. 6. "Free" dielectric constants of sodium chlorate and sodium bromate.

mode was controlled by the elastic constant $c_{44}{}^E=1/s_{44}{}^E$, and that an accurate measurement free from width correction can be obtained by measuring the frequencies of high harmonics.

Table I shows the frequency constant of the three sets of crystals for sodium chlorate taken over the temperature range. The frequency constant listed is a product of the frequency determining direction (the length for the two longitudinal crystals and the width for the shear crystal), measured at 25°C, by the frequency of vibration. Since the frequency of vibration is given by the formula

$$f=\frac{1}{2l}\left(\frac{1}{\rho s^E}\right)^{\frac{1}{2}} \tag{11}$$

and $f_c=fl_0$ where l_0 is the length measured at 25°C, the elastic constant s^E is given by the formula

$$\begin{aligned} s^E &= \frac{1}{\left(2f_c\dfrac{l}{l_0}\right)^2\rho} \\ &= \frac{1}{[2f_c(1+\alpha(\Theta-25))]^2\dfrac{\rho_0}{[1+\alpha(\Theta-25)]^3}}, \qquad (12) \\ &= \frac{1+\alpha(\Theta-25)}{(2f_c)^2\rho_0}, \end{aligned}$$

where α is the temperature coefficient of the length which is the same for all directions of a cubic crystal. The temperature expansions of sodium chlorate and bromate crystals have been measured[5] from −50°C to +110°C and are plotted as a percent expansion from 25° by the curves of Fig. 4. Since this represents a small correction to the elastic constant, the curves have been extrapolated up to the highest temperature used.

As the temperature increased, it was found that the dielectric and piezoelectric constants also increased. At 200°C the leakage resistance of the crystal became noticeable and became low enough at 210°C and higher to make the measurement of the dielectric constant and the antiresonant frequency unreliable. The resistivity

TABLE II. Elastic compliances and piezoelectric constants of sodium chlorate.

Temperature in °C	Expansion of length compared to length at 25°C	Value of $s_{11}{}^{E'}$ for 22.5° crystal	Value of $s_{11}{}^{E'}$ for 45° crystal	Value of $s_{44}{}^E$	Value of piezoelectric constant g_{14}	Value of piezoelectric constant h_{14}	Value of f_{14}	Value of d_{14}
28	1.000	2.69×10^{-12} cm²/dyne	3.045×10^{-12}	8.54×10^{-12}	13.7×10^{-8}	1.61×10^{4}	8.75×10^{4}	$6.2\times10^{-}$
40	1.00055	2.705	3.075	8.60	14.6	1.69	8.85	6.6
75	1.00215	2.825	3.175	8.86	16.2	1.83	8.75	7.6
100	1.0033	2.895	3.265	9.05	17.8	1.96	8.75	8.5
130	1.0047	3.005	3.360	9.30	19.9	2.14	8.8	9.9
140	1.00512	3.038	3.402	9.41	20.8	2.22	8.78	10.4
150	1.00557	3.080	3.445	9.49	22.1	2.34	9.05	11.2
160	1.00604	3.130	3.49	9.56	23.2	2.42	9.05	11.9
170	1.00647	3.185	3.525	9.72	24.4	2.52	9.10	12.7
180	1.00695	3.205	3.565	9.85	25.6	2.60	9.10	13.5
190	1.0074	3.255	3.62	10.00	27.6	2.77	9.20	14.8
200	1.00787	3.305	3.675	10.13	29.8	2.94	9.40	16.2
210	1.00832	3.360	3.735	10.3				
220	1.00877	3.402	3.795	10.48				
230	1.00925	3.482	3.882	10.71				
240	1.00967	3.565	3.96	10.93				

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[5] This measurement was made by Miss E. J. Armstrong.

curve as a function of temperature is shown plotted by Fig. 5. At 245°C the resistivity was low enough so that no appreciable piezoelectric response was obtained and, at the melting point of 263°C, the resistivity was less than 1000 ohms per cubic centimeter. This indicates that as the crystal approaches its melting point, it becomes highly ionized with the chlorate ion separating from the sodium ion for a large number of molecules. This behavior is usual for an ionic crystal.

Table I shows also the ratio $\Delta f/f_R$ for the 45° cut, and the free dielectric constant measured at 1000 cycles, as a function of temperature. These quantities were measured with the crystals in holders for which all stray capacities were tied to ground and since the impedances in the measuring circuits were low, these can be neglected. Hence no corrections had to be made and the measured results are given directly. From the data given in Table I, all the constants can be evaluated. The data for the dielectric constants of sodium chlorate and sodium bromate are shown plotted in Fig. 6. The dielectric constant can be expressed as a function of temperature by the empirical equation

$$\epsilon = 4.7 + \frac{310}{320-\Theta} - \frac{6750}{(320-\Theta)^2}. \qquad (13)$$

This indicates that there is a part equal to 4.7 that is independent of temperature and another part that varies with temperature and becomes large for temperatures approaching 320°C. The first part is caused by the electronic and ionic polarizabilities while the temperature variable part is caused by changes in orientation of dipoles or to displacement of loosely bound ions such as exist in glass. This happens more freely as the temperature increases. Since no adequate treatment of the dielectric constant has been made for temperatures below a transition point, an empirical formula has to be resorted to in order to locate the temperature transition point. For sodium bromate, since the measured values are taken considerably below the transition point, a single term is sufficient to fit the curve and we have

$$\epsilon = 4.87 + \frac{(323)}{(414-\Theta)}. \qquad (14)$$

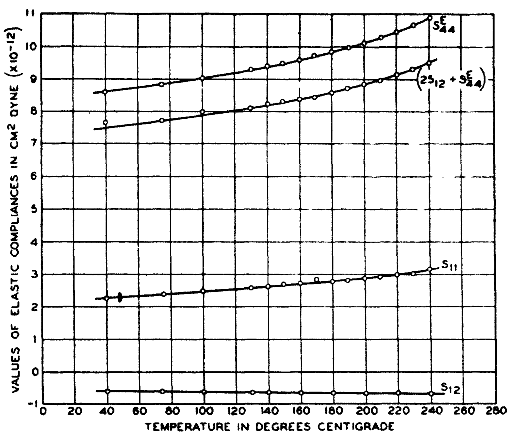

FIG. 7. Elastic compliances of sodium chlorate.

Table II shows a calculation of the elastic compliances of the three crystals shown in Table I. Since the value of $s_{11}^{E'}$ as a function of the orientation for a crystal cut normal to Z can be written

$$s_{11}^{E'} = s_{11}(\sin^4\varphi + \cos^4\varphi) + (2s_{12}+s_{44}^E)\sin^2\varphi\cos^2\varphi,$$

the values of s_{11} and $(2s_{12}+s_{11}^E)$ are given by

$$\begin{aligned} s_{11} &= 2s_{11}^{E'}{}_{22.5°} - s_{11}^{E'}{}_{45°}, \\ (2s_{12}+s_{44}^E) &= 6s_{11}^{E'}{}_{45°} - 4s_{11}^{E'}{}_{22.5°}. \end{aligned} \qquad (15)$$

Since s_{44}^E is evaluated in column 5 of Table II, all three elastic constants can be determined and they are shown plotted by Fig. 7. Since the elastic constant s_{44}^D is related to s_{44}^E by the equations

$$s_{44}^D = s_{44}^E - g_{14}^2\epsilon_1^T/4\pi, \qquad (16)$$

it can be evaluated from the data of Table II and Fig. 7. It differs from s_{44}^E by too small an amount to plot on the curve and hence is not shown.

The only previous data is that published by Voigt[2] who found

$$\begin{aligned} s_{11} &= 2.46\times10^{-12}\ \text{cm}^2/\text{dyne}, \\ s_{12} &= +1.252\times10^{-12}, \\ s_{44} &= 8.36\times10^{-12} \end{aligned} \qquad (17)$$

at room temperature. These data resulted in a negative Poisson's ratio (one which causes the cross-sectional dimensions to increase as the

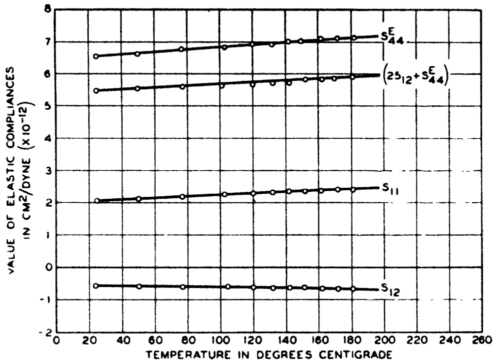

FIG. 8. Elastic compliances of sodium bromate.

length increases) of -0.51, a point that was stressed by Voigt. The present data, however, do not support this conclusion for the value of s_{12} found is negative giving a Poisson's ratio of 0.23, which is an ordinary value to be expected.

The values of the piezoelectric constants g_{14} and h_{14} are given by the sixth and seventh columns. Since the Voigt piezoelectric constant d_{14} (relating the piezoelectric strain to the applied field) is related to g_{14} by

$$d_{14}=g_{14}\frac{\epsilon_1{}^T}{4\pi}, \qquad (18)$$

the value of d_{14} at room temperature is 6.1×10^{-8}, which is somewhat larger than Pockels' value of 4.84×10^{-8}.

We note from Table II that both g_{14} and h_{14} increase considerably as the temperature rises. To test whether the piezoelectric strain is proportional to that part of the polarization which varies with temperature, use is made of Eq. (5) and the data on the dielectric constant given in Eq. (11). The resulting value of f_{14} is shown in the next to the last column and within the experimental accuracy is a constant 9×10^4. This indicates that there is a one to one correspondence between the rotation of the dipoles in the unit cell and the shear stress on the unit cell.

Similar measurements have been made on three sodium bromate crystals cut with the same orientations with respect to the crystallographic axes. The dielectric constant as a function of temperature is shown by Fig. 6. This variation satisfies the formula

$$\epsilon^T=4.87+323/(414-\Theta). \qquad (14)$$

Since the melting point is known to be about 400°C, this indicates again that if there is a Curie temperature it is near the melting point. The three elastic compliances are shown plotted in Fig. 8. They show a linear variation and do not have the curvature of sodium chlorate since the temperature is farther from the melting point. The piezoelectric constants are shown by Fig. 9. From these data it can be shown that the piezoelectric constant f_{14} is independent of the temperature and equal to 18×10^4. It is over twice as large as the constant for sodium chlorate.

IV. DISCUSSION OF RESULTS

From the experimental data obtained it appears possible to conclude that the dielectric constant is made up of a part which is relatively temperature independent and another part that varies nearly inversely as the difference between a temperature θ, possibly a Curie temperature, and the actual temperature. However the dielectric constant data place this Curie temperature above the melting point. The fact that one component of the dielectric constant varies with temperature indicates that this component may be caused by dipoles that become unfrozen as the temperature increases. This polarization might be caused by an actual rotation of the dipoles as is usually assumed, or it might be caused by an inversion of the position of the chlorine in the chlorate ion as has been found to occur in the similar nitrate ion NO_3. Either assumption would give a component of the polarization that varied with temperature. There is no reason to suppose, however, that the temperature of an apex inversion would be in any way connected with the melting point, whereas if the component is caused by an actual rotation of the dipoles, the dipoles might well become free rotationally at about the same temperature that they become free translationally. At that tem-

TABLE III. Comparison of the dipole piezoelectric effect in four crystals.

Material	f_{14}	Electromechanical coupling factor at 25°C
KH_2PO_4	3×10^4	0.11
$NH_4H_2PO_4$	16×10^4	0.29
$NaClO_3$	9×10^4	0.03
$NaBrO_3$	18×10^4	0.04

perature all the free dipoles could show a cooperative effect and hence a dielectric Curie point, so that the evidence seems to point to an actual rotation of the dipoles as the cause of the temperature variable part of the polarization. The temperature independent part of the dielectric constant is presumably caused in part by electronic polarization of the component sodium, oxygen, and chlorine of the molecules. Since the square of the refractive index of both salts is about 2.5 there is also an appreciable temperature independent polarization caused presumably by displacements of the lattice ions. At present there is no adequate theory for connecting the number of molecules per cc and the average dipole moment per molecule with the susceptibility of a solid below a Curie point.

The measurements of the piezoelectric constant given in Section III show conclusively that the gross distortion of the lattice under an applied charge (the piezoelectric effect) is directly proportional to that portion of the polarization which varies with temperature, i.e., the part due to change in orientation of the dipoles. A comparison of this dipole piezoelectric effect, which has been measured for four crystals, is shown by Table III. This table shows that this constant varies for different crystals by a factor of about 6 to 1 being highest for sodium bromate and lowest for potassium dihydrogen phosphate. The next column shows the value of the electromechanical coupling factor which is a measure of the amount of the total applied electrical energy that appears in mechanical form under static conditions. An examination of the data shows that this is low for sodium chlorate and sodium bromate because the electronic and ionic polarization is large compared to the dipole polarization and hence only a small fraction of the total input electrical energy goes into orienting the dipoles. KDP which has a smaller dipole piezoelectric constant has a larger electromechanical coupling because of the fact that the dipole polarization represents about three fourths of the total polarization, whereas for sodium chlorate it is only 0.2 of the total. Ammonium dihydrogen phosphate obtains its large coupling because of the fact that over fifty percent of the total polarization is dipole polarization and in addition the dipole piezoelectric constant is large.

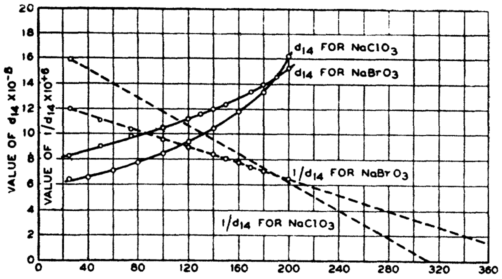

FIG. 9. Piezoelectric constants d_{14} for $NaClO_3$ and $NaBrO_3$ as a function of temperature.

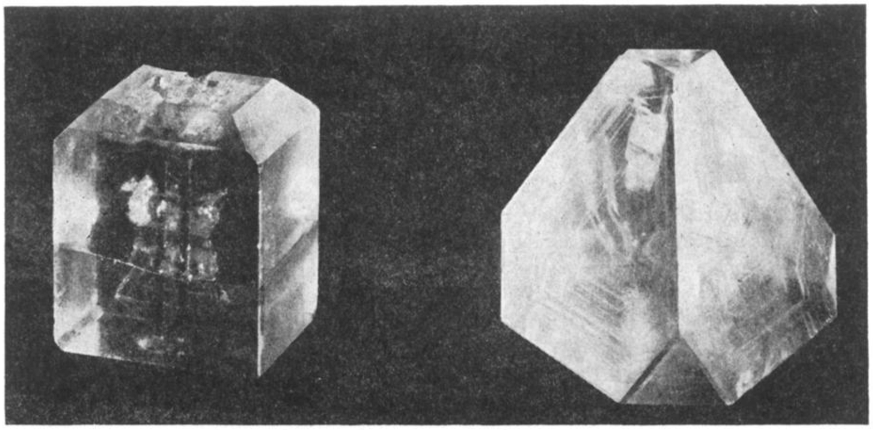

FIG. 3. Photograph of sodium chlorate crystal (left) and sodium bromate crystal (right).