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Temperature Dependence of the Elastic Constants of Monocrystals of Sodium Chloride and Silver Chloride

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Results are reported of the measurement of the elastic constants of single crystals of sodium chloride and silver chloride in the temperature range from room temperature to the melting point.

1. THE present research is the extension of earlier work[1-4], in which the properties of halide compounds of silver and thallium were investigated. In it we report the results of the determination of the elastic constants of single crystals of silver chloride and sodium chloride at temperatures ranging from room temperature to the melting temperature.

The method of measuring the constants is as follows[5-7]. A long rod of amorphous quartz is attached to a piezoquartz. To the rod in turn there is attached the sample to be investigated (such a system we call a triple oscillator in the following). Mechanical vibration of the oscillator is produced by applying a variable electrical potential to the piezoquartz crystal. By an investigation of the condition for resonance of the triple oscillator we could determine the eigenfrequency of the sample under investigation, and the elastic constants were calculated from this frequency. At a temperature of 577°C, the piezoquartz loses its piezoelectric property (transition $\alpha \rightarrow \beta$ quartz). In view of this fact, the piezoquartz and the specimen were separated in high temperature experiments by a sufficiently long rod of fused quartz (or similar material), so that the piezoquartz could be at room temperature while the specimen was at an arbitrary high temperature.

The oscillator consisting of the piezoquartz and the specimen is called a double oscillator. Measurements with the use of a double oscillator are possible only at temperatures below 577 °C.

The reactive impedance between the electrodes of the piezoquartz contains a part which depends on the amplitude of the mechanical vibration. This amplitude is given by the expression

$$a = \frac{V_0 F(y_1, y_2, y_3)}{\Delta}; \qquad (1)$$

here V_0 is the amplitude of the applied voltage;

$$y_i = \pi \frac{\nu_0}{\nu_1}\left[1 + \frac{1}{2}\pi^2\mu_i^2\left(\frac{I_i}{\rho_i l_i^2}\right)\left(1 - \frac{\nu^2_0}{\nu_i^2}\right)\right], \qquad (2)$$

where ν_i are the characteristic frequencies, μ_i the Poisson's ratios, l_i the lengths, I_i the moments of inertia of the cross section relative to the axis of symmetry, ρ_i the densities, ν_0 the characteristic frequency of the triple oscillator. $F(y_1, y_2, y_3)$ is a function practically independent of ν_0 in a sufficiently wide frequency range in the neighborhood of ν_0. In what follows we denote the various

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[1] A. V. Stepanov, Z. Phys. Sowjetunion 6, 313 (1934).

[2] A. V. Stepanov, Z. Phys. Sowjetunion 8, 25 (1935).

[3] A. V. Stepanov, Zh. Tekhn. Fiz. 19, 205 (1949).

[4] B. M. Krasnov and A. V. Stepanov, J. Exper. Theoret. Phys. USSR 25, 98 (1953).

[5] L. Hunter and S. Siegel, Phys. Rev 61, 84 (1942).

[6] F. C. Rose, Phys. Rev. 49, 50 (1936).

[7] M. Durand, Phys. Rev. 50, 449 (1936).

parts by $i = 0$ for the composite oscillator: $i = 1$ for the specimen; $i = 2$ for the piezoquartz; $i = 3$ for the amorphous rod;

$$\Delta = \frac{m_1 \operatorname{tg} y_1}{y_1} + \frac{m_2 \operatorname{tg} y_2}{y_2} + \frac{m_3 \operatorname{tg} y_3}{y_3} - \frac{m_1 m_2}{m_3} \frac{y_3}{y_1 y_2} \operatorname{tg} y_1 \operatorname{tg} y_2 \operatorname{tg} y_3. \tag{3}$$

The characteristic frequencies ν_i are given by the expression

$$\nu_i = n \left(\frac{M^{1/2}}{2\rho_i^{1/2} l_i} \right) \left(1 - \frac{\pi^2 n^2 \mu_i^2 I_i}{2 l_i^2 \rho_i} \right), \tag{4}$$

where n is an integer (the number of the harmonic), M is Young's modulus or the shear-modulus in a direction parallel to the axis of the specimen. The term

$$\frac{\pi^2 n^2 \mu^2 I_i}{2 l_i^2 \rho_i} \tag{5}$$

of Eq. (4) takes into account the lateral deformation of the specimen.

In the measurements described below, Eq. (5) enters as a small correction in the calculation of the dimensions of all arrangements of the triple oscillator. Because of the size of experimental errors, we have neglected terms of the form (5) in all our calculations. The calculation of the characteristic frequencies in Eq. (4) is then based on the expression

$$\nu_i = \frac{n}{2l_i} \sqrt{\frac{M}{\rho_i}}. \tag{6}$$

It follows from Eq. (1) that the condition for resonance (i.e., coincidence of the electrical vibration frequency and the frequency of the characteristic mechanical vibration of the composite oscillator, ν_0) is defined by the relation

$$\frac{m_1 \operatorname{tg} y_1}{y_1} + \frac{m_2 \operatorname{tg} y_2}{y_2} + \frac{m_3 \operatorname{tg} y_3}{y_3} - \frac{m_1 m_2}{m_3} \frac{y_3}{y_1 y_2} \operatorname{tg} y_1 \operatorname{tg} y_2 \operatorname{tg} y_3 = 0. \tag{7}$$

If ν_0, ν_1, ν_2 and ν_3 are sufficiently close to each other, then

$$\frac{\operatorname{tg} y_1}{y_1} = \frac{1}{\nu_0} \left[\frac{m_2}{m_1} (\nu_2 - \nu_0) + \frac{m_3}{m_1} (\nu_3 - \nu_0) \right], \tag{8}$$

or, if we denote the right hand side of Eq. (8) by a,

$$\operatorname{tg} \pi \frac{\nu_0}{\nu_1} = a\pi \frac{\nu_0}{\nu_1}\,[*] \tag{9}$$

The dependence of ν_0/ν_1 on a is found graphically.

The determination of the modulus at high temperatures is made by means of Eq. (6), in which a correction is made for the thermal expansion. The correction is made both for the length l and the density ρ, after which Eq. (6) takes the form

$$M = \frac{4 l^2 \rho \nu_1^2}{n^2 \left(1 + \frac{\Delta l}{l}\right)}, \tag{11}$$

where $\Delta l / l$ is the relative extension of the specimen in the temperature interval from room temperature to the temperature of measurement.

The temperature dependence of the frequency ν_1 of the quartz rod was taken into account in the calculation of the frequency of the specimen ν_3.

The formulas were developed for the case in which the specimen, piezoquartz and quartz rod all have cylindrical shape, and are valid for longitudinal vibrations of cylindrical and rectangular specimens and for torsional vibrations of cylindrical specimens. For the case of torsional vibrations of specimens of rectangular cross section, the formulas differ only by a factor in front of the term $1 - \frac{\nu_0^2}{\nu_i^2}$ in Eq. (2) [**], but the order of magnitude of this multiplier remains the same. The origin of this factor is similar to that of the remaining term in Eq. (4).

All measurements of torsional vibrations were carried out on specimens of rectangular cross section.

Calculation of the shear modulus was made from Eq. (11), with a correction for the fact that the cross section does not remain plane in the torsion of a specimen of rectangular cross section[2].

In this case we can use the formula which is valid for isotropic material provided that the axis of torsion of the crystalline specimen has a sym-

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[*] If $\nu_0 = \nu_1 = \nu_2 = \nu_3$, the approximate relation

$$\nu_1 = \nu_0 + \frac{m_2}{m_1} (\nu_0 - \nu_2) + \frac{m_3}{m_1} (\nu_0 - \nu_3) \tag{10}$$

is satisfied.

[**] This term is generally absent for torsional vibrations of cylindrical specimens. See reference 6.

metry higher than third order. This condition was satisfied in our measurements, since the measurements (of torsional vibrations) were carried out on specimens which were oriented along the axis of a cube [100]. With the correction term added, Eq. (11) has the form

$$G_{[100]} = \frac{4{,}77 l_0^2 \nu_1^2 \rho}{n^2}. \tag{13}$$

Here G_{100} is the shear modulus for a specimen whose axis coincides with the [100] direction[+].

Two types of oscillators were employed in the research: a double oscillator for the measurements at room temperature, and a triple for measurements at elevated temperatures. Some of the oscillators were used for longitudinal vibrations, some for torsional.

The piezoquartz for the longitudinal vibrations were in the form of bars of square cross section 3×3 mm^2, length 27 mm (frequency ~ 100 kc), cut along the mechanical axis. Silver electrodes were attached to the faces perpendicular to the electric axis. The piezoquartz for the torsional vibrations were in the form of cylinders of diameter 3 mm, length 27 mm (frequency ~ 75 kc), whose axes coincided with the electric axis. Electrodes were attached to the generating cylinder, which was perpendicular to the bisector of the angle between the optical and mechanical axes.

The length of the quartz rod was ~ 500 mm, and was so adjusted that the frequency of the system: piezo-quartz rod was equal, within 0.5%, to that of the piezoquartz alone.

The specimens of sodium chloride and silver chloride examined were either square (3×3 mm^2) or circular ($d \approx 3$ mm) in cross section. The length of the specimen ranged from 10 to 20 mm.

Electrical vibrations were produced by a standard signal generator. This generator was frequency calibrated to within 0.05%. An EO-4 oscilloscope, inserted in the diagonal of the bridge fed by the standard signal generator, served as an indicator of resonance. The piezoquartz formed one arm of this bridge; another arm was a variable capacitance, which was so adjusted that the bridge was in equilibrium in the absence of resonance.

Measurement of the frequency of the triple oscillator was carried on during slow heating of a furnace. The time required for these measurements was small in comparison with the time necessary for a measurable change in the temperature of the oscillator. From this point of view, the measurements during the heating process were justified. Only in experiments at temperatures close to the melting point of the crystal under measurement were the measurements carried out in the steady state.

Cementing of the parts of the oscillator was one of the most critical operations. The cementing spot had to be very strong, heat resistant, and thin, in order that it present no obstacles to the measurement. For cementing, we used a mixture of water glass and $CaCO_3$ in the form of a thin powder. In the case of temperature measurement with NaCl four days drying were allowed; for AgCl, two days drying. The cementing mixture did not have to be very thick. The cementing was carried out in a special arrangement which guaranteed the matching and pressing together of all the cemented parts.

The quartz rods were cemented to the piezoquartz; then the quartz rod was shortened until the frequency of the entire system was within 0.5% of the frequency of the piezoquartz[‡].

The frequency of the quartz rod ν_3 enters into the calculated formula (9) for the determination of the frequency ν_1 of the specimen. For this

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[+] As is known[8],

$$\nu_n = \frac{u}{2l} \sqrt{\frac{N_s}{I_p \rho}}, \tag{12}$$

where N_s is the static torsional coefficient I_p is the polar moment of inertia of the cross section of the specimen. For a specimen of square cross section with side a, $I_p = a^4/6$, $N_s = \alpha a^4 G$, $\alpha = 0.14$, G = shear modulus. Substituting the values of I_p and N_s in Eq. (13).

[8] W. Cady, *Piezoelectricity*.

[‡] In this case the frequency of the quartz rod was close to the frequency of the piezoquartz, since the mass of the quartz rod was appreciably greater that that of the piezoquartz, and therefore the frequency of the system piezoquartz + rod was close to that of the quartz rod than to the frequency of the piezoquartz. Let ν_2 be the frequency of the piezoquartz, ν_0' the frequency of the system piezoquartz + rod, ν_3 the frequency of the quartz rod. Then, from Eq. (1), which is written for the double oscillator,

$$\nu_3 = \nu_0' + \frac{m_3}{m_3}(\nu_0' - \nu_2), \tag{14}$$

where m_2 is the mass of the piezoquartz, m_3 the mass of the quartz rod.

TABLE I

Sodium Chloride

t °C	s_{11}, $10^{-12}\frac{\text{cm}^3}{\text{dyne}}$	s_{44}, $10^{-12}\frac{\text{cm}^3}{\text{dyne}}$	s_{12}, $10^{-12}\frac{\text{cm}^3}{\text{dyne}}$	$\varkappa$, $10^{-12}\frac{\text{cm}^3}{\text{dyne}}$
20	2.28	7.60	—0.26	4.40
100	2.52	7.82	—0.51	4.50
150	2.67	7.94	—0.61	4.35
200	2.81	8.14	—0.71	4.16
250	2.98	8.34	—0.81	4.10
300	3.16	8.46	—0.89	4.14
350	3.36	8.70	—1.00	4.10
400	3.58	8.84	—1.06	4.37
450	3.82	9.08	—1.11	4.50
500	4.08	9.34	—1.21	4.98
550	4.36	9.52	—1.24	5.64
600	4.70	9.70	—1.35	6.00
650	5.10	10.00	—1.46	6.54
700	5.55	10.20	—1.55	7.35
750	6.10	10.40	—1.58	8.82
780	6.58	10.50	—1.73	9.36
790	6.67	10.62	—1.78	9.33
800	6.75	10.62	—1.71	9.99
804	6.85	10.62	—1.76	9.99

TABLE II

Silver Chloride

t °C	s_{11}, $10^{-12}\frac{\text{cm}^3}{\text{dyne}}$	s_{44}, $10^{-12}\frac{\text{cm}^3}{\text{dyne}}$	s_{12}, $10^{-12}\frac{\text{cm}^3}{\text{dyne}}$	$\varkappa$, $10^{-12}\frac{\text{cm}^3}{\text{dyne}}$
20	3.15	16.25	—1.08	3.00
100	3.79	16.50	—1.21	4.10
125	4.13	16.60	—1.33	4.40
150	4.41	16.70	—1.40	4.83
175	4.69	16.80	—1.45	5.36
200	4.88	17.00	—1.43	5.75
225	5.05	17.20	—1.43	6.57
250	4.21	17.35	—1.39	7.30
275	5.40	17.60	—1.20	9.00
300	5.52	18.25	—1.05	10.30
325	5.65	19.05	—0.97	11.10
350	5.78	19.80	—0.88	12.10
375	5.92	20.07	—0.70	12.80
400	6.06	22.20	—0.76	13.60
425	6.29	23.80	—0.95	13.50
435	6.41	24.50	—0.90	13.80
445	6.58	25.30	—1.23	12.35
450	6.71	25.80	—1.41	11.90
455	6.90	26.20	—1.48	11.80

reason, the temperature dependence of the frequency of the quartz rod (without the specimen) was first measured in the same position in the furnace as in the subsequent measurements with the specimen. The dependence of the frequency of the double oscillator: piezoquartz + quartz rod $\nu_0'(T)$, was recorded and the temperature dependence of the frequency ν_3 of the quartz rod was determined.

The frequency of the quartz rod changed very slightly with change in temperature. Measurements were carried out for all oscillators used in the research[++]

After the preliminary investigation of the system piezoquartz + quartz rod, the specimen under investigation was attached. The necessary length of the specimen was chosen earlier on the double oscillator at room temperature (the specimen was attached directly to the piezoquartz). The dependence of the frequency of the system ν_0, on the length of specimen l was determined. The length of the specimen was then changed by abrasion or by cutting, and the specimen length l_0 was selected for which the frequency of the specimen, ν_1, was equal to the frequency of the piezoquartz, ν_2. Usually a specimen of length somewhat different from l_0 was attached to the system piezoquartz + quartz rod. As a result, the whole cycle of temperature measurements could be carried out on the specimen without cutting it.

Measurements of the cross section of the specimens was obtained to within 0.01 mm. The lengths of the specimens were measured by a comparator with accuracy to within 0.03 mm. The accuracy of the determination of the orientation of the crystals was within 1° (in the case of pitting of specimens by cleavage it was higher). The value of the resonance frequency was measured on the generator scale to within 0.05%. The temperature in the furnace was measured with a platinum platinum-rhodium thermocouple by the compensation method. Measurements were accurate to within 1 °C.

The temperature gradient in the oven in the part where the specimen was located was about 0.3 degrees /cm.

Density data for sodium chloride, silver chloride and quartz were taken from tables of physical constants.

The coefficients of expansion and their temperature dependence (i.e., the values of $\Delta l/l$ in Eq. (11) for crystals of sodium chloride and silver chloride were taken from references 9, 10. The frequency of the piezoquartz in a temperature interval from 20° to 35°C remained constant within the limits of accuracy of the apparatus. The accuracy of the measurement of the elastic moduli at room temperature was of the order of 1% with the double oscillator. The accuracy of measurement of the elastic moduli at high temperatures with the triple oscillator was within 10% for silver chloride and 5% for sodium chloride.

3. Measurements were made of the temperature dependence of the eigenfrequency of the samples of sodium chloride and silver chloride in the interval from room temperature to the melting temperature with the aid of triple oscillators.

The measurements were made in the case of longitudinal vibrations with specimens oriented along the directions [100] and [110], and for torsional vibrations with specimens oriented in the [100] direction. For crystals of sodium chloride and silver chloride, the temperature dependence of Young's modulus was measured in the [100] and [110] directions ($E_{[100]}$ and $E_{[110]}$) and the shear modulus was measured in the [100] direction in the temperature interval from room temperature to the melting point. All specimens had square cross sections in these experiments. Measurements of $E_{[100]}$ and $G_{[100]}$ for sodium chloride were obtained in two steps, with cutting of the specimen. In all other cases the measurements were made without cutting of the sample.

The constants s_{11}, s_{44} and s_{12} were computed from known relations[11] on the basis of the data obtained. The results are shown in Tables I and II. The values of the compressibility $\varkappa$, computed from the data for S_{ik}, are also given in the tables.

The results in Table I show that our data for

[++] The resonant frequencies of the system piezoquartz + quartz rod were close to one another. This is explained by the fact that the resonance frequencies of the quartz rod were close to one another (because of high number of the harmonic), and since the mass of the quartz rod underwent a transition from one harmonic to another, the frequency of the whole system underwent a small change

$$\nu_0' = \frac{\nu_3 m_3 + \nu_2 m_2}{m_3 + m_2}, \qquad (15)$$

where $\nu_3 m_3$ is the principal term $m_3 \gg m_2$.

[9] P. G. Strelkov, A. K. Val'ter and V. P. Gachkovskii, J. Exper. Theoret. Phys. USSR 7, 519 (1937).

[10] P. G. Strelkov, V. P. Gachkovskii, J. Exper. Theoret. Phys. USSR 1, 231, 243 (1931).

[11] W. Voigt, *Lehrbuch der Kristallphysik*, Teubner, 1910.

sodium chloride are in agreement, within experimental errors, with the results of other authors[5,12]. The measurements for silver chloride at room temperature are in agreement with those of Arenberg[13].

As is seen from Table II, a significant decrease in the compressibility of silver chloride was observed at temperatures close to the melting point.

A detailed investigation was carried out for sodium chloride[5]. In our measurements we did not observe such an effect for sodium chloride, evidently because of the insufficient accuracy of the method.

It is also evident from the results that the Cauchy relation $\frac{c_{11}}{c_{44}} = 1$ is satisfied approximately for sodium chloride crystals in the temperature interval investigated. In the case of silver chloride the ratio c_{11}/c_{44} is a function of the temperature and is approximately unity only for temperatures close to the melting point. From this it follows that the Cauchy condition is not universal, and can be satisfied only in a limited temperature range.

In conclusion, we consider it our duty to express our gratitude to E. M. Evstaf'ev for a series of valued instructions on the method of investigation, and to A. L. Shakh-Budagov for criticism of the results and for the great help during the course of the work.

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[12] A. E. Briukhanov, J. Exper. Theoret. Phys. USSR 9, 722 (1939).

[13] D. L. Arenberg, J. Appl. Phys. 21, 941 (1950).

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