

THE ELASTIC CONSTANTS OF NaCl AT 77.3°K AND 4.2°K

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Abstract—The adiabatic elastic constants of NaCl have been measured at 77.3°K and 4.2°K using the ultrasonic pulse echo technique. The results are as follows (in units of 10^{11} dyne cm^{-2}):

	C'_{11}	C'	C_{44}
77.3°K	4.807	2.272	1.335
4.2°K	4.850	2.321	1.337

where $C'_{11} = \frac{1}{2}(C_{11} + C_{12} + 2C_{44})$ and $C' = \frac{1}{2}(C_{11} - C_{12})$. These values have been used to calculate the adiabatic bulk modulus and to re-evaluate the low temperature value of the Gruneisen parameter as determined from thermal expansion data and microscopic mode gammas.

INTRODUCTION

ANHARMONICITY in crystals is usually considered in the light of the Quasi Harmonic Model.⁽¹⁾ In using this model, one expands the potential energy in terms of the displacements of the atoms or ions from their equilibrium positions, keeping only terms to second order. By considering the free energy in this approximation and by using thermodynamic relations, one arrives at the Mie-Gruneisen equation of state

$$\gamma_G = \frac{\beta B_s}{C_p/V}, \quad (1)$$

where γ_G is known as the Gruneisen parameter [defined by equation (1)], β is the volume coefficient of thermal expansion, B_s is the adiabatic bulk modulus, and C_p/V is the heat capacity per unit volume. The Quasi Harmonic Model also leads to a value of γ_G in terms of the microscopic parameters γ_i defined by

$$\gamma_i \equiv -\frac{d \ln \omega_i}{d \ln V}, \quad (2)$$

where the ω_i depend only on the volume and correspond to the normal mode frequencies. Defined in this way the γ_i are a measure of the anharmonicity of a crystal.

The calculation of γ_G in the region of low temperature requires a precise determination of not only β and C_p but also B_s . WHITE⁽²⁾ has recently determined β for NaCl from which he calculates γ_G (denoted as γ_0 in his work) in the T^3 region of temperature and in this calculation has used the value of B_s as reported by OVERTON and SWIM.⁽³⁾ A plot of Overton and Swim's B_s vs. temp. leads one to believe that their values are low. Furthermore, the corresponding low temperature gamma reported by BARTELS and SCHUELE,⁽⁴⁾ $\bar{\gamma}_L$ (calculated from the γ_i) is some 17% greater than White's γ_0 . Hence this work was undertaken to measure the elastic constants of NaCl at very low temperatures and thereby redetermine B_s . Furthermore, it was of interest to test the supposition of Bartels and Schuele that a change of the value of B_s at low temperatures would not appreciably change their calculated value of the low temperature $\bar{\gamma}_L$. Finally, it was considered advantageous to determine low temperature elastic data on samples from the same parent crystal that provided samples for the pressure data collected by Bartels and Schuele.

EXPERIMENTAL PROCEDURE

Sample preparation

Two NaCl single crystals were prepared from one-in. cleavage cubes obtained from the Harshaw Chemical Company. One of the crystals was oriented with its ends normal to the [110] direction by mounting the cleavage

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cube in an appropriate steel fixture and lapping the protruding edges with water on a felt covered motor driven turntable. The other crystal was oriented with its ends normal to the [100] direction and required no special orientation fixture since the cleavage cube was of the desired orientation. After rough shaping, both crystals were mounted in steel lapping rings, and the end surfaces were ground flat and parallel on fine grit emery paper backed by plate glass. The final shapes of the two crystals were approximate right circular cylinders with diameters of about 1.7 cm for the [110] sample and 1.3 cm for the [100] sample and with lengths (at 22°C) of 1.9068 cm and 2.2873 cm, respectively.

Measurements

Figure 1 shows the assembly used to hold the NaCl samples for low temperature measurements. This assembly, surrounded by a stainless steel jacket not

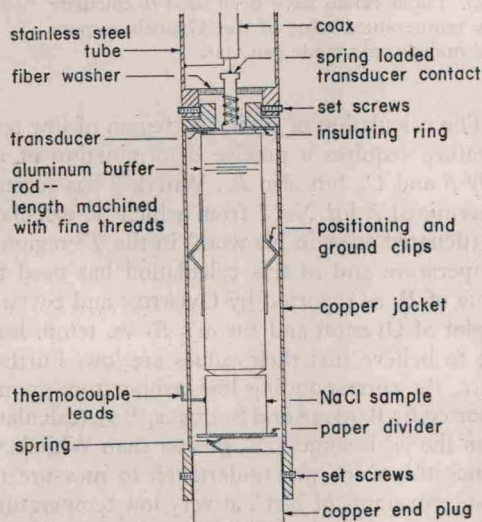


FIG. 1. Arrangement used to hold NaCl samples for low temperature measurements.

shown, was held in a double jacketed dewar, the inner jacket being equipped with a special cap so that the cryogenic liquid could be introduced slowly, thus permitting a slow rate of cooling (about 2°K per min from 295°K to 77.3°K and about 1°K per min from 77.3°K to 4.2°K). The temperature of the sample was determined by means of a copper-constantan thermocouple referenced at 0°C in an air saturated ice bath. A Leeds and Northrup potentiometer Type K-2 and a Leeds and Northrup D-C Null Detector model 9834 were used to measure the thermocouple voltage.

The fundamental measurements involved in this work were the transit times of 10 Mc/s acoustic pulses. (Transit time is defined as the time required for the pulse to traverse the length of the sample twice.) The pulse echo method was used, and a good description of

measurements of this kind may be found in earlier papers from this laboratory.⁽⁶⁾ The system used in the present work was based on a Tektronix type 547 variable delay oscilloscope equipped with a Type 1A1 plug-in unit. The oscilloscope was modified by replacing the sweep delay helipot by a more linear ($\pm 0.015\%$ linearity) helipot in combination with external resistance boxes. In this way, any fraction of the total sweep time could be put on the helipot, which allowed a more sensitive measurement of the time between successive echoes. The portion of the helipot used for each run was calibrated after each run with one microsecond time marks from a Tektronix TM180A time mark generator. The 10 Mc/s pulses were generated by an Arenberg model PG-650c pulse generator, and reflected signals were first amplified with an Arenberg model PA-260 pre-amplifier before being displayed on the oscilloscope.

An aluminum buffer rod (shown in Fig. 1) was used in all measurements. Glycerin was found to be an ideal seal material between the transducer and aluminum rod. A mixture of 50% isopentane and 50% rubber cement solvent was found to be a satisfactory seal material for the NaCl crystals. This 50-50 mixture begins to solidify (in the form of a glassy state) at about 90°K and undergoes all major phase changes by 77.3°K. The 50-50 mixture is very volatile at room temperature and thus an airtight seal of rubber cement was painted around the end of the NaCl crystal where it was in contact with the aluminum buffer rod. Rubber cement was tried once as a seal material on the [100] crystal. However, in cooling down from 77.3°K to 4.2°K, the strain caused by differential contraction cleaved the [100] crystal rather seriously. On no occasion did the 50-50 mixture seals cause cleaving of the NaCl crystals.

In measuring the transit times, only the first three echoes were used. The first echo is referred to as the first buffer echo since it comes from the buffer rod-NaCl crystal interface. The next two echoes (the first and second crystal echoes) come from transmissions through the crystal. These three echoes should be spaced at intervals of the transit time of the sample under investigation. The transit time was measured by recording the reading of the helipot for several cycles of one echo and then recording the helipot readings of the corresponding cycles in the next echo. In order to insure that the corresponding cycles were measured, special double exposure photographs were taken. This was done by aligning a particular cycle with a vertical line on the oscilloscope screen, making an exposure, and then aligning what was thought to be the corresponding cycle of the next echo with the same vertical line on the oscilloscope and then making another exposure without moving the film. The amplitudes of the corresponding cycles were set equal by means of the variable gain on the oscilloscope. If the corresponding cycle was chosen correctly the photograph showed two echo patterns almost exactly superimposed upon one another. It was clearly evident, however, if the corresponding cycle was chosen improperly because of the large amplitude discrepancies between the corresponding cycles of the two echoes. This photographic method has also proven

valuable in detecting the predicted phase change that exists between the second crystal echo and the buffer and first crystal echoes. (For aluminum and NaCl this phase inversion exists for all wave modes and crystal polarizations.) The double exposure photographs have also shown that a relative phase change sometimes occurs between two echoes and that this phase change increases or decreases as a function of position through the echo. This phase change was sometimes corrected by slightly altering the frequency of the pulse generator.

It is to be emphasized that the sample and seals were not disturbed during the transfer from liquid nitrogen to liquid helium. Furthermore, double exposure photographs (one exposure taken at 77.3°K and one at 4.2°K) showed that the wave shapes of the echoes did not change.

RESULTS

The quantity measured in this work was the transit time T of 10 Mc/s pulses in the crystals. From the transit time the velocity v of the wave is given by

$$v = \frac{2L}{T}, \quad (3)$$

where L is the length of the crystal. The elastic constant C_i is then given by

$$C_i = \rho v_i^2 = \rho \frac{4L^2}{T_i^2}, \quad (4)$$

where ρ is the density of the crystal. Since ρ and L change with temperature, these quantities had to be calculated at 77.3°K and 4.2°K and appear in Table 1 with other basic data used in calculating the results. The three elastic

stiffnesses for cubic crystals of [110] orientation are $C'_{11} = \frac{1}{2}(C_{11} + C_{12} + 2C_{44})$, $C' = \frac{1}{2}(C_{11} - C_{12})$ and C_{44} , corresponding to the three waves velocities, one longitudinal and two transverse. Although a [100] crystal was prepared, it was cleaved badly during a helium run and the data taken with this crystal is thought not to be reliable, except for the C_{11} mode at 77.3°K. Table 2 lists the velocities, elastic constants and adiabatic bulk moduli at 77.3°K and 4.2°K for the [110] crystal.

The length of the crystal at 295°K given in Table 1 is the average of 53 measurements made with a Starrett micrometer. The room temperature length of the crystal did not change during the sequence of runs to determine C'_{11} , C_{44} and C' . A back reflection Laue was taken to determine the crystal orientation ($\phi = 44^\circ 56'$, $\theta = 90^\circ 00'$); correction for this slight misorientation appear in the sixth place.

As explained above, the transit time measurements consisted of recording the helipot reading for several corresponding cycles in two successive echoes. This was done for the buffer-first crystal echoes and for the first-second crystal echoes. The precision of transit times measured in this way depends on several factors. The uncertainty due to the inability of the experimenter to set the helipot and due to the instability of the electronic equipment was not more than 0.05%. However, as mentioned above, the phase between two successive echoes sometimes changed slightly, creating different transit times between different parts of the echoes. These phase changes were not always

Table 1. Basic data used in elastic constant calculations. The values at 77.3°K and 4.2°K are calculated from thermal expansion data⁽⁶⁾ and the values at 295°K. An Avogadro's number of 6.02305×10^{23} was used in calculating the density

	295°K	77.3°K	4.2°K
Molecular weight	58.448 ⁽⁴⁾		
Lattice constant (angstroms)	5.6393 ⁽⁷⁾	5.5983	5.5953
X-ray density (g cm ⁻³)	2.1644	2.2123	2.2159
Linear coefficient of thermal expansion (10 ⁻⁶ deg ⁻¹)	39.9 ⁽⁶⁾	19.7	0.01
Length crystal A [110] (mm)	19.068	18.930	18.920
Isothermal bulk modulus (10 ¹¹ dyne cm ⁻²)	2.339 ⁽⁴⁾		

Table 2. Adiabatic elastic stiffnesses of NaCl at 77.3°K and 4.2°K. $C'_{11} = \frac{1}{2}(C_{11} + C_{12} + 2C_{44})$; $C' = \frac{1}{2}(C_{11} - C_{12})$; and $B_s = \frac{1}{3}(C_{11} + 2C_{12})$. C'_{11} , C' and C_{44} are directly measured quantities on the [110] crystal

Mode		Longitudinal	Transverse	Transverse	Adiabatic bulk modulus ² B_s
Polarization		110	110	001	
Elastic constant designation		C'_{11}	C'	C_{44}	
77.3°K	Velocity ¹	4.661	3.205	2.457	2.715
	Elastic constant ²	4.807	2.272	1.335	
4.2°K	Velocity ¹	4.678	3.236	2.457	2.739
	Elastic constant ²	4.850	2.321	1.337	

¹ (10^5 cm/sec).

² (10^{11} dyne cm^{-2}).

present and never produced an uncertainty greater than 0.1%. The reproducibility of the transit time for any one given mode and polarization was found to be on the order of 0.2% or less. This result includes measurements made with different buffer rods (silica and other aluminum rods) and different seal materials (measurements involving different seal materials were made at 77.3°K only).

Even though there was good consistency between the buffer-first crystal time and between the first-second crystal time separately, the two transit times did not always agree. Where there was disagreement, the time between the two crystal echoes was greater by as much as 0.2% than the time between the buffer and first crystal echoes. This phenomenon has been observed previously in this laboratory and investigations to explain it are being planned. In this work only the transit time given by the buffer-first crystal echoes was used in calculating the elastic constants. The choice is based primarily on the fact that photographs of the leading edge of the second crystal echo showed a slight amount of signal mixing of the echo with spurious 10 Mc/s signal probably due to mode conversion and scattering off the side walls of the crystal and buffer rod. On occasions when the spurious signal appeared to be absent the two transit times were nearly in agreement. Considering the above factors plus the errors introduced in the thermal expansion calculations, it is thought that the absolute uncertainty of the elastic constants in Table 2 is no

more than 0.5%. A measurement of C_{11} was obtained from the [100] crystal at 77.3°K prior to its cleaving, and it agrees with the value of C_{11} calculated from the [110] crystal data to better than 0.02%. Furthermore, even though the low temperature elastic constants determined from the [100] crystal are thought not to be reliable, they agree to within 0.3% of those elastic constants determined from the [110] crystal.

Table 3 shows a comparison of the 4.2°K elastic constants with other investigators. Comparison of these results with the recent work of LEWIS *et al.*⁽⁸⁾ appears to be slightly outside the limits of uncertainty placed on the measurements, which suggests some sort of systematic effect. Measurements on the [110] crystal were made at room temperature using Salol as the seal material and the results agree with those of BARTELS and SCHUELE.⁽⁴⁾ To compare various methods of measurement a series of materials have been measured in this laboratory using the buffer rod method and in the Olin Laboratory for Materials at Case using the pulse overlap method,⁽⁹⁾ and agreement is found to be better than 0.1%.

LOW TEMPERATURE GRUNEISEN PARAMETER

WHITE⁽²⁾ has measured the low temperature thermal expansivity of NaCl and at sufficiently low temperatures assumes the data can be fit to a

Table 3. Comparison of 4.2°K elastic constants and adiabatic bulk modulus in units of 10^{11} dyne cm^{-2}

Investigator	C_{11}	C_{12}	C_{44}	B_s
Authors	5.834	1.192	1.337	2.739
LEWIS <i>et al.</i> ⁽⁸⁾	5.733	1.123	1.331	2.660
OVERTON and SWIM ⁽³⁾	5.750	0.986	1.327	2.574

power series with the leading term being proportional to T^4 , which gives a T^3 leading term to the linear expansion coefficient. Coupling this result with the Debye temperature, θ_D , the molar volume, V , and the bulk modulus, B_s , he calculates the Gruneisen parameter γ_0 corresponding to the low temperature T^3 region. White used the bulk modulus determined by OVERTON and SWIM⁽³⁾ with the result that $\gamma_0 = 0.90 \pm 0.03$. The present measurement of the bulk modulus is 6.6% higher than Overton and Swim's value and increases γ_0 to 0.96 ± 0.03 .

In terms of the microscopic parameters⁽¹⁰⁾ of the crystal, the Gruneisen parameter is given by

$$\gamma = \frac{\sum_i c_i \gamma_i}{\sum_i c_i}, \quad (5)$$

where c_i is the Einstein heat capacity of the i^{th} normal mode. In the T^3 region of temperature, one may assume the crystal to behave like an elastic continuum with the weighting factors in the above expression being replaced by $C_i^{-3/2}$, the elastic constant for the i^{th} branch in the direction θ , ϕ , and the above equation goes over to the

following integral form

$$\bar{\gamma}_L = \frac{\sum_{i=1}^3 \int \gamma_i C_i^{-3/2} d\Omega}{\sum_{i=1}^3 \int C_i^{-3/2} d\Omega} \quad (6)$$

where $d\Omega$ is the element of solid angle. The γ_i for low frequency modes can be calculated from the pressure derivatives of the elastic constants as described by various authors.⁽¹⁰⁾ The above integral has been calculated for temperatures of 295°K and 195°K using the low temperature elastic constants reported in Table 3 along with the pressure data of BARTELS.⁽⁴⁾ These results, along with a volume extrapolation to 0°K as predicted by the Quasi Harmonic Approximation, are listed in Table 4. Bartels obtained an extrapolated value of 1.05, using Overton and Swim's low temperature elastic data, as compared to the authors' value of 1.06. There are two main reasons why $\bar{\gamma}_L$ was insensitive to the changes in the low temperature elastic constants. First, the weighting factors occur in both the numerator and denominator in the expression for $\bar{\gamma}_L$ and thus a slight change

Table 4. $\bar{\gamma}_L$ for NaCl calculated from the mode gammas compared with White's Thermodynamic value of γ_0

	295°K	195°K	0°K	White
$\bar{\gamma}_L$	1.17	1.12	1.06	0.96 ± 0.03
$\frac{V_{295} - V}{V_{295}}$	0	0.0112	0.0232	

The values of $\bar{\gamma}_L$ listed under 295°K and 195°K were calculated from the mode gammas at those temperatures and were 'volume extrapolated' to give the value listed under 0°K. This latter value can be considered to be calculated from the 0°K mode gammas and is the one that should be compared with White's value. Also given are the relative volume changes that were used. V is the volume at the temperature under consideration and V_{295} is the volume at 295°K.

in them tends to cancel. Second, the transverse mode corresponding to C_{44} carries the largest weighting since it is the lowest velocity mode, and the measured value of C_{44} reported by Overton and Swim differs with the authors' value by less than one per cent.

The Debye temperature, θ_D , can be calculated from the value of the integral which appears in the denominator of the expression for $\bar{\gamma}_L$. The data of Overton and Swim gives a value of 322.3°K, while the present data yields a value of 322.0°K. This slight effect upon θ_D is due to the fact that the dominant mode in determining θ_D is C_{44} .

The main effect of the present measurements has been to increase the low temperature bulk modulus and also the measured low temperature Gruneisen parameter by about 7%, while leaving the calculated Gruneisen parameter, $\bar{\gamma}_L$, essentially unchanged.

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REFERENCES

1. LEIBFRIED G. and LUDWIG W., *Solid St. Phys.* (editors SEITZ F. and TURNBULL D.) **12**, 275. Academic Press, New York (1961).

2. WHITE G. K., *Proc. R. Soc.*, **A286**, 204 (1965).
 3. OVERTON W. C. and SWIM R. T., *Phys. Rev.* **84**, 758 (1951).
 4. BARTELS R. A. and SCHUELE D. E., *J. Phys. Chem. Solids* **26**, 539 (1965).
 5. DANIELS W. B. and SMITH C. S., *The Physics and Chemistry of High Pressures*, p. 50. Soc. of Chem. Industry, London (1963).
 6. MEINCKE P. P. M. and GRAHAM G. M., *Eighth Int. Conf. on Low Temp. Phys.* (to be published).
 7. *National Bureau of Standards Circular* **539**, 2, 41 (1953).
 8. LEWIS J. T., LEHOCZKY A. and BRISCOE C. V., *Bull. Am. Phys. Soc.* Vol. **10**, no. 1, p. 44.
 9. MCSKIMIN H. J., *J. Acoust. Soc. Am.* **33**, 12 (1961).
 10. SHEARD F. W., *Phil. Mag.* **3**, 1381 (1958).

Note added in proof—P. P. M. MEINCKE and G. M. GRAHAM [*Can. J. Phys.* **43**, 1853 (1965)] recently reported thermal expansion data on NaCl. Their technique involves the use of a Fabrey-Perot etalon dilatometer and for NaCl in the region below 12°K they fitted their experimental points with $\alpha = 6.1 \pm 0.1 T^3/^\circ K$; which results in a $\gamma_0 = 1.06$. Using the authors' bulk modulus data raises their value of γ_0 to 1.13.