PRESSURE AND TEMPERATURE DEPENDENCE OF THE ELASTIC CONSTANTS OF LiBr AND LiCl

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ABSTRACT

Measurements of the pressure and temperature dependence of the second order elastic constants of LiBr and LiCl single crystals have been made by the ultrasonic interferometric technique at temperatures from 220 to 340°K, and pressures up to 3.5 kbars. The adiabatic elastic constants (in units of 10^{11} dynes/cm²) and the isothermal pressure derivative of the adiabatic constants (unitless) at 295°K are as follows (where $C_{00} = \frac{1}{2}[C_{11} + C_{12} + 2C_{44}]$):

	C_{11}	C_{44}	C_{00}	$\frac{dC_{11}}{dP}$	$\frac{dC_{44}}{dP}$	$\frac{dC_{00}}{dP}$
LiBr	3.959	1.909	4.843	10.42	1.68	8.27
LiCl	4.963	2.503	6.124	10.42	1.70	8.34

The three measured quantities C_{11} , C_{44} , and C_{00} are given respectively by ρv_{11}^2 , ρv_{44}^2 , and ρv_{00}^2 where ρ is the density and the v 's are the sound velocities at a specific pressure and temperature. The Debye temperatures are calculated from the second order elastic constants at four temperatures on the interval 220 to 340°K.

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INTRODUCTION

In recent years there have been a number of theoretical treatments of the cohesion of alkali halide crystals with a view to elaborating and extending the original, and quite successful, Born model.^{1,2} Since the model only involves central forces in a centrosymmetric lattice, the Cauchy relations therefore must hold at $T = 0^\circ\text{K}$. Careful measurements of elastic constants indicate that these relations fail to be satisfied at room temperature and the failure is also often marked at low temperatures.

The quasiharmonic approximation developed by Leibfried and Hahn^{3,4} can be used to calculate the temperature dependence of the elastic constants. In this approximation the failure of the Cauchy relations at finite temperatures follows as a consequence of the vibrational free energy of the crystal. Nanyan⁵ and Ghate⁶ have used such a quasiharmonic model for the calculation of the third order elastic constants and their temperature variation. Recently Lincoln, Koliwad and Ghate⁷ have included the van der Waals interaction in their calculation of the second and third order elastic constants of some NaCl type alkali halides. The second order elastic constants and their pressure derivatives provide convenient tests of the theories of cohesion. The pressure derivatives of the second order elastic constants are related to the higher order elastic constants which in turn are related to the anharmonicity of the lattice.

In the present article, the experimental values of the deformed-state second order elastic constants of LiBr and LiCl and their pressure derivatives in the temperature range from 220°K to 340°K will be presented. The theoretical values computed by R. C. Lincoln and P. B. Ghate will be compared with the experimental values.

EXPERIMENTAL PROCEDURE

1. Sample Preparation

Cylindrical ingots of LiBr and LiCl of approximately half inch diameter and two inches long were obtained from the Cornell Ionic Crystal Growing Laboratory with longitudinal axes in the [100] and [110] directions. Each crystal was cut into two pieces of dimension 1" x 1/2" x 1/2" by a string saw, using water as the cutting fluid. The deviation from the exact orientation was measured to within a few hundredths of a degree by using an x-ray diffractometer; the faces of the crystal were then ground towards the desired orientation by handlapping on a glass plate using successively finer grades of Clover Lapping Compound. Because these salts are hygroscopic, all the further sample preparations were carried out in a dry box in an argon gas atmosphere. The pair of opposite faces were ground parallel to within 1×10^{-4} inches. The 10 MHz x- and y-cut quartz transducers, obtained from Valpey Crystal Corporation, were of the coaxial type, 3/8" in diameter, with a central active area of 1/4" in diameter. The transducers were bonded to the crystals with Nonaq Stopcock Grease for temperatures between 220°K and 260°K and glycerin for temperatures between 260°K and 340°K. The transducer bonded samples were mounted in a specially designed crystal holder.⁸ Three crystals bonded with the following transducers were studied simultaneously at pressure,

Crystal face orientation	(100)	(100)	(110)
Transducer	x-cut	y-cut	x-cut
Elastic Constant	C_{11}	C_{44}	$C_{00} =$ $(C_{11} + C_{12} + 2C_{44})/2$

Because these crystals are highly hygroscopic, it was decided to use no pure modes which required orientation of the transducer on the crystal face in a direction normal to the wave propagation direction, inasmuch as this would require considerable additional exposure of the crystal during x-ray orientation. Consequently, instead of measuring a second shear constant [$C' = (C_{11} - C_{12})/2$], a second longitudinal constant C_{00} was studied. The accuracy and reproducibility of the resultant data justifies this approach.

2. Transit Time Measurement

The ultrasonic phase comparison technique originally developed by Williams and Lamb⁹ was used to measure the transit time of the acoustic pulses. The 10 MHz carrier signal was provided by a Hewlett-Packard 606A signal generator. An Arenberg 650C pulse oscillator was modified by the manufacturer to provide the high power phase coherent r.f. pulses needed. The receiving system consisted of an Arenberg PA 620 preamplifier of variable gain and input impedance, an Arenberg WA-600 wideband amplifier and a Tektronic 545A oscilloscope with a fast rise time preamplifier module. A block diagram of the electronic system is shown in Figure 1. To make a measurement, the output

stage of the 650C was tuned to the resonance at 10 MHz and the input coils on the preamplifier were adjusted to resonate with the transducer capacitance and the stray wiring capacitance. The delay potentiometer was then adjusted so that the pulses overlap, after which the amplitude of the delayed signal was adjusted to minimize the amplitude of the sum at the same time that the carrier frequency was varied. The frequencies of five nulls around the transducer resonance frequency were measured at each experimental point. Maximum sensitivity was achieved by operating at maximum gain and with the maximum pulse width possible. If the pulse shapes were good, the null frequencies were repeatable to 20 Hz, although in the worst circumstances an uncertainty of 100 to 200 Hz existed. Thus the sensitivity of the system was better than 2 parts in 10^5 .

3. Pressure and Temperature Systems

A gas bench designed to generate approximately 14 kbar gas pressure was available. Briefly, it consists of a gas operated compressor, a hydraulically operated pressure intensifier, a separator, a hydraulic pump and associated valves, gauges, and interconnections. A schematic diagram is shown in Figure 2. The pressure vessel¹⁰ was made of maraging steel. The gas inlet tubing was soldered into the end plug while four electric leads were threaded out through the other end plug which incorporated an armoured Bridgman seal. The pressure was transmitted from the gas bench to the vessel via 1/8" O.D. hard drawn 304 stainless steel tubing.

Temperature control of the system was achieved by putting

the vessel in a temperature chamber (Model MK 6300 manufactured by Delta Design Inc.) with working range from 100°K to 600°K and of $\pm 0.2^\circ\text{K}$ accuracy. The gas pressure was measured by a Heise gauge which was calibrated to ± 10 bars.

DATA ANALYSIS

Elastic constants at each pressure were evaluated using the transit length at that pressure. In general the adiabatic elastic constants C_{00}^S , C_{44} , and C_{11}^S (the superscript s means adiabatic) have the form

$$C^S(P) = \rho_0 \ell_0^2 S \frac{1}{\tau^2} \quad (1)$$

where S and τ are functions of pressure and ρ_0 and ℓ_0 are the density and transit length at zero pressure. Here S is defined by

$$S = \frac{\ell_0}{\ell(P)} \quad (2)$$

The values of S are obtained from Cook's expression.¹¹ In the present case

$$S = 1 + \frac{1}{4\rho_0} \int_0^P \frac{1 + \Delta}{\left\{ \frac{\ell_{000}^2}{\tau_{00}^2} \right\} - \left\{ \frac{\ell_{044}^2}{\tau_{44}^2} \right\} - \frac{1}{4} \left\{ \frac{\ell_{011}^2}{\tau_{11}^2} \right\}} dP \quad (3)$$

where

$$\Delta = \frac{T\beta^2 B^S}{C_P \rho} ,$$

B^S = adiabatic bulk modulus = $(C_{11}^S + 2C_{12}^S)/3$,

β = volume thermal expansion coefficient,

C_p = specific heat at constant pressure,

ρ = density of the crystal,

T = temperature in degrees Kelvin,

l_{000} , l_{044} , l_{011} are the sample lengths at zero pressure

corresponding to $C_{00}^S = (C_{11} + C_{12} + 2C_{44})/2$, C_{44} , and C_{11}^S ,

τ_{00} , τ_{44} , and τ_{11} are the transit times at pressure.

To evaluate Δ at pressure we use the following thermodynamic expressions:

$$\left(\frac{\partial \beta}{\partial P}\right)_T = - \left[\frac{\partial}{\partial T} \left\{ \frac{1}{B^S} \right\} \right]_P \quad (4)$$

$$\begin{aligned} \left(\frac{\partial C_p}{\partial P}\right)_T &= - T \left[\frac{\partial^2}{\partial T^2} \left\{ \frac{1}{\rho} \right\} \right]_P, \\ &= - \frac{T}{\rho} \left[\frac{\partial \beta}{\partial T} + \beta^2 \right]_P. \end{aligned} \quad (5)$$

The specific heat data for LiCl (NBS¹²) and LiBr (the theoretically computed values of Arnold M. Karo¹³) have been used in the above calculation. The densities at 295°K have been taken to be 2.0753 gm/cm³ for LiCl and 3.4708 gm/cm³ for LiBr.¹⁴ The corrections to the transit lengths were made by using the thermal expansion data of F. A. Henglein;¹⁵ in addition approximate values of $\partial \beta / \partial T$ were obtained from this data.

RESULTS AND DISCUSSION

Absolute values of the adiabatic elastic constants and bulk moduli at zero pressure and at different temperatures are

given in Tables I and II. The pressure derivatives obtained by a least square fit are listed in Tables III and IV.

The accuracies of the experimentally measured quantities are: α : $\pm 0.02\%$, ρ : $\pm 0.03\%$, P : $\pm 0.1\%$, τ : $\pm 0.002\%$.

The accuracies of the directly measured adiabatic elastic constants (C_{11} , C_{44} , and C_{00}) listed in this article are:

adiabatic elastic constants $\pm 0.1\%$,

pressure derivatives $\pm 3\%$.

Inasmuch as B^S is obtained by difference, errors in B^S and dB^S/dP may be larger.

The main features of these results for LiCl and LiBr are:

At atmospheric pressure the adiabatic elastic constants decrease linearly as temperature increases over the temperature range studied.

The adiabatic elastic constants vary linearly with pressure.

The pressure derivatives of the effective elastic constants increase as the temperature increases.

Second and third order elastic constants of LiBr and LiCl have been calculated by R. C. Lincoln¹⁶ and P. B. Ghate⁶ using the Born model of ionic solids. In this model the coulomb potential is of the form A/R and the short range repulsive potential is of the form $B \exp(-R/b)$ with interactions up to the second-nearest neighbors. Temperature variations of the elastic constants are developed by using the quasiharmonic approximation. The comparison between theoretical and experimental values of

second order elastic constants and their pressure derivative is given in Table V. The agreement is fair except in the case of $\frac{dC_{44}}{dP}$.

The temperature dependence of the elastic constants of LiCl at one atmosphere has been investigated by Marshall et al.¹⁷ from 4.2 to 300°K, and by Haussühl¹⁸ from 238 to 373°K. The values of the atmospheric pressure elastic constants at 295 and 220°K obtained in the present work and given in References (17,18) are shown in Table VI. This shows the near agreement between the present work and the values reported by Haussühl. The present values for C_{11} and C_{12} do not agree with those of Marshall et al. We note that the Cauchy relation, $C_{12}=C_{44}$, is approximately satisfied for LiBr whereas in the case of LiCl, $C_{12} < C_{44}$. The Love relation, $\frac{dC_{12}}{dP} - \frac{dC_{44}}{dP} = 2$, is not satisfied in either case.

The temperature variation of $\frac{dB^T}{dP}$ is shown in Figure 3. It varies linearly in this temperature range.

Debye Temperature

The Debye temperature can be calculated from the following formula,¹⁹

$$\theta = \frac{h}{k} \left(\frac{9}{4\pi} \frac{N}{V} \right)^{1/3} \left[\int \left(\frac{1}{C_1^3} + \frac{1}{C_2^3} + \frac{1}{C_3^3} \right) \frac{d\Omega}{4\pi} \right]^{-1/3} \quad (6)$$

where

N = number of atoms per unit cell,

V = volume of the unit cell,

C_1, C_2, C_3 = sound velocities of different modes (one longitudinal and two transverse).

Perhaps the simplest and most commonly used method of calculating θ makes use of tables prepared by de Launay.²⁰ The tables are prepared in terms of ratios of elastic constants and yield a function f . Then θ is obtained from the equation

$$\theta = \frac{h}{k} \left(\frac{9N}{4\pi V} \right)^{1/3} \left(\frac{C_{44}}{\rho} \right)^{1/2} \left(\frac{9}{18 + \sqrt{3}} f \right)^{1/3}. \quad (7)$$

The resultant values at four temperatures are given in Table VII.

Table I

Temperature Dependence of Adiabatic Elastic
Constants of LiBr*

T(°K)	C_{11}^S	C_{44}^S	C_{00}^S	B^S	B^T
219.15	4.267	1.977	5.067	2.698	2.537
238.70	4.188	1.959	5.010	2.672	2.504
260.00	4.099	1.940	4.947	2.643	2.469
285.55	3.997	1.917	4.871	2.606	2.424
303.00	3.929	1.902	4.820	2.581	2.395
319.50	3.860	1.887	4.769	2.556	2.365
337.00	3.787	1.871	4.716	2.531	2.336

*All elastic constants are in units of 10^{11} dynes/cm².

Table II

Temperature Dependence of Adiabatic Elastic
Constants of LiCl*

T(°K)	C_{11}^S	C_{44}^S	C_{00}^S	B^S	B^T
220.44	5.303	2.578	6.370	3.288	3.134
246.67	5.186	2.552	6.283	3.246	3.084
259.16	5.124	2.539	6.242	3.229	3.064
283.15	5.018	2.515	6.163	3.191	3.019
302.66	4.927	2.495	6.099	3.163	2.984
327.40	4.815	2.469	6.014	3.122	2.937
339.50	4.759	2.457	5.975	3.104	2.916

*All elastic constants are in units of 10^{11} dynes/cm².

Table III

Temperature Dependence of Pressure Derivatives
of Elastic Constants of LiBr*

T(°K)	219.15	260.00	303.00	337.00
$(dC_{11}^S/dP)_0$	10.30	10.36	10.43	10.49
$(dC_{11}^T/dP)_0$	10.36	10.38	10.40	10.42
$(dC_{44}/dP)_0$	1.55	1.61	1.68	1.73
$(dC_{00}^S/dP)_0$	7.87	8.09	8.31	8.48
$(dC_{00}^T/dP)_0$	7.93	8.11	8.28	8.41
$(dB^S/dP)_0$	5.00	5.19	5.36	5.50
$(dB^T/dP)_0$	5.06	5.21	5.33	5.43

* All pressure derivatives are dimensionless.

Table IV

Temperature Dependence of Pressure Derivatives
of Elastic Constants of LiCl*

T(°K)	220.44	259.16	302.66	339.50
$(dC_{11}^S/dP)_0$	10.35	10.38	10.43	10.47
$(dC_{11}^T/dP)_0$	10.37	10.37	10.39	10.39
$(dC_{44}/dP)_0$	1.59	1.65	1.71	1.76
$(dC_{00}^S/dP)_0$	8.04	8.19	8.37	8.52
$(dC_{00}^T/dP)_0$	8.06	8.18	8.33	8.44
$(dB^S/dP)_0$	5.15	5.26	5.40	5.52
$(dB^T/dP)_0$	5.17	5.25	5.36	5.44

* All pressure derivatives are dimensionless.

Table V

Comparison of Theoretical and Experimental Results (295°K)*

Sample		C_{11}^T	C_{12}^T	C_{44}	dC_{11}^T/dP	dC_{12}^T/dP	dC_{44}/dP
LiBr	Theoretical	4.010	1.520	1.743	10.17	2.12	0.12
	Experimental	3.775	1.725	1.909	10.40	2.77	1.67
LiCl	Theoretical	4.407	2.102	2.340	9.32	2.25	0.25
	Experimental	4.787	2.103	2.503	10.39	2.81	1.70

*All elastic constants are in units of 10^{11} dynes/cm² and all pressure derivatives are dimensionless.

Table VI

Comparison of Results*

Sample	T(°K)		C_{11}^S	C_{12}^S	C_{44}
LiBr	295	Haussühl	3.94	1.87	1.93
		Present Work	3.958	1.908	1.909
LiCl	295	Haussühl	4.94	2.28	2.46
		Present Work	4.963	2.277	2.503
		Marshall et al.	4.848	1.890	2.470
LiCl	220	Present Work	5.305	2.281	2.578
		Marshall et al.	5.131	1.807	2.539

*All elastic constants are in units of 10^{11} dynes/cm².

Table VII

Calculated Debye Temperatures ($^{\circ}\text{K}$) at
Indicated Temperatures

LiBr		LiCl	
T	θ	T	θ
219.15	256.84	220.44	403.39
260.00	251.73	259.16	396.64
303.00	246.29	302.66	389.46
337.00	241.67	339.50	382.50

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Figure 1: Block diagram of the electronic system.

Figure 2: Mark II Gas Bench

Figure 3: Temperature Dependence of $\left(\frac{dB^T}{dP}\right)_{P=0}$ of LiBr and LiCl.

Figure 2