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Elastic Constants of the Alkali Halides at 4.2°K†

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Adiabatic elastic constants of LiCl, NaF, NaCl, NaBr, KF, RbCl, RbBr, and RbI were measured at 4.2 and 300°K, using the ultrasonic pulse-echo technique. Data are also given for several of these materials, for the temperature interval 4.2 to 300°K. It is observed that the elastic anisotropy factor, $A=2c_{44}/(c_{11}-c_{12})$, increases with temperature. This results in the Li halides becoming less anisotropic and the Na, K, and Rb halides becoming more anisotropic as the temperature decreases toward $T=0$°K. The Cauchy relation ($c_{12}=c_{44}$) is not satisfied at 4.2°K for any of the materials studied. The degree of failure of the Cauchy relation ($\Delta=c_{12}-c_{44}$) is larger at 4.2°K than at room temperature for the Li and Na halides but is smaller for the K and Rb halides. Also calculated was the $T=0$°K value Θ_0^{el} of the Debye characteristic temperature from the 4.2°K elastic-constant data, using the tables given by de Launay. The values of Θ_0^{el} in °K are: LiCl (429±2.2), NaF(491.5±2.4), NaCl(321.2±1.6), NaBr(224.6±1.2), KF(335.9±1.7), RbCl(168.9±0.85), RbBr(136.5±0.7), and RbI(108.0±0.55). Comparison with Θ_0^c the Debye characteristic temperature derived from low-temperature specific-heat data, shows the two to be equal within experimental error in almost all cases. However, there is some indication of a trend toward Θ_0^{el} being larger than Θ_0^c by an amount on the order of 1 to 3%. Whether this trend is real or the result of some systematic error in the experiments or analysis is not known at this time.

INTRODUCTION

The elastic constants of solids, correlated with other physical properties, provide a valuable insight into the nature of atomic binding forces. Low-temperature values of elastic constants are especially useful as a basis for semiempirical force models or as a final check of fundamental theories of lattice dynamics.

The adiabatic elastic constants of LiCl, NaF, NaCl, NaBr, KF, RbCl, RbBr, and RbI have been determined at room temperature and at 4.2°K. Measurements on some of these materials have been made between 4.2 and 300°K and for these cases the temperature dependence of the elastic constants is given. An attempt to determine the elastic constants of LiBr was made but the samples cracked on three separate occasions when cooled to 77.3°K. The 4.2°K data for NaF, NaCl, and NaBr has been reported at an APS meeting by Lewis *et al.*[1] At a later APS meeting Lehoczky *et al.*,[2] presented the low-temperature elastic constants of LiCl, KF, and RbCl.

Including the work reported in this paper the elastic constants of 13 of the 16 alkali halides in the Li, Na, K, and Rb halide series have been measured at 4.2°K. The materials excluded are LiBr, LiI, and RbF. The majority of the previous work was done at the William Marsh Rice University in Houston, Texas. Briscoe and Squire[3] determined the elastic constants of LiF, Norwood and Briscoe[4] made measurements on KCl and KI, and Claytor and Marshall[5] did the low-temperature work on NaI. Prior to this, Galt[6] in 1948 made low-temperature measurements on KBr. Recently Fugate and Schuele[7] reported values for the elastic constants of NaCl at 77.3 and 4.2°K. Other measurements have been made for NaCl in the vicinity of liquid-nitrogen temperature. Overton and Swim,[8] using the pulse-echo technique, determined the elastic constants of NaCl from 60 to 300°K. Rose[9] made earlier measurements on NaCl from 80 to 300°K using a "composite oscillator" technique.

Numerous measurements of the elastic constants of the alkali halides have been reported for room temperature. We will mention only the work of Haussühl[10] and of Bergmann[11] who have determined the elastic constants at room temperature for most of the alkali halides studied in this research.

Theoretical calculations of the elastic constants of the alkali halides are many. We will refer to the work of Löwdin,[12] Krishnan and Roy,[13] Karo,[14] Dick,[15] and Mitskevich.[16] The works of Löwdin and Dick are primarily concerned with the failure of the Cauchy relation ($c_{12}=c_{44}$) and report the quantity $\Delta=c_{12}-c_{44}$ (the degree of failure of the Cauchy relation). These

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theories will be compared with experiment in the later sections of this paper.

At low temperatures the specific heat of a dielectric solid is determined by low-energy, long-wavelength lattice vibrations. The elastic constants, determined at 4.2°K from the measured velocity of low-frequency acoustical waves, can be used to compute the characteristic Debye temperature,[17–21] hereafter referred to as Θ_0^{el}. Comparison of Θ_0^{el} will be made with Θ_0^{c}, the Debye characteristic temperature determined from low-temperature specific-heat data.

Several other physical quantities, which are useful in the characterization of the properties of solids, may be related to the low-temperature elastic constants. In addition to Θ_0^{el} and Δ mentioned above we have tabulated and discussed the low-temperature values of the compressibility, β, the infrared lattice resonance frequency, ω_0, and the elastic anisotropy constant, A. When it is of interest the temperature dependence of the above quantities is also presented.

EXPERIMENTAL

The samples used were high purity, optically clear, single crystals. The LiCl, RbCl, RbBr, and RbI specimens were obtained from Semi-Elements, Inc., Saxonburg, Pennsylvania. The NaF, NaCl, NaBr, and KF samples were purchased from the Harshaw Chemical Company, Cleveland, Ohio. The sample dimensions were approximately 1 in.×0.75 in.×0.75 in. The 0.75-in.×0.75-in. faces were perpendicular (to within ±2°) to either the [100] or the [110] crystallographic direction.

The single crystals were polished on a lint-free cotton cloth stretched tightly over a piece of plate glass. The cloth was saturated with a mixture of ethylene glycol and either 700 or 1300 grit polishing powder. The samples were polished until the 0.75-in. ×0.75-in. faces were parallel to within 0.6 mrad and flat to approximately 5 parts in 10^4. A dial gauge with a least count of 5×10^{-5} in. was used to indicate the irregularities in the crystal surfaces. The length of the specimens was determined using a precision micrometer with a least count of 10^{-4} in.

In general the alkali halides are hygroscopic. Several of the materials studied in this research were hygroscopic to such an extent that it was necessary to do all sample preparation in a dry atmosphere. The crystals of NaF, NaCl, NaBr, RbCl, and RbBr could be safely prepared under normal humidity conditions. However, it was necessary to handle LiCl, KF, and RbI in a "dry box" and to avoid any prolonged exposure to normal atmospheric conditions.

The elastic constants were determined from sound velocity measurements made using the well known pulse-echo technique.[22] The following relations were used in calculating the elastic constants from the measured velocities of 1 to 2 μsec unrectified 10 MHz pulses:

$$\rho v_l^2 = c_{11}, \tag{1}$$

where v_l is the velocity of a longitudinal wave propagating in the [100] crystallographic direction;

$$\rho v_t^2 = c_{44}, \tag{2}$$

where v_t is the velocity of a transverse wave propagating in the [100] crystallographic direction; and

$$\rho v_l^2 = \tfrac{1}{2}(c_{11}+c_{12}+2c_{44}), \tag{3}$$

where v_l is the velocity of a longitudinal wave propagating in the [110] crystallographic direction. In the above expressions, ρ is the density of the material.

The measurement of sound velocity, using the pulse-echo technique, necessitates the coupling of energy generated by electromechanical transducers (x- and y-cut quartz crystals) into the specimen being studied. This is accomplished by physically bonding the transducers to the sample with an adhesive. At reduced temperatures this presents a problem because of the differential thermal contraction between the quartz transducer, the adhesive, and the easily cleaved alkali halide specimens. In this work a mixture of approximately 64% propylene, 33% methane, and 3% nitrogen applied at 77°K served as a satisfactory bonding agent for work down to 4.2°K. A more detailed account of the equipment and procedure used has been published.[23]

Except for 4.2°K, temperature measurements were made using a copper-Constantan thermocouple referenced to 0°C and calibrated at 77.4°K.

RESULTS AND DISCUSSION

The pulse-echo technique of measuring elastic constants requires a knowledge of the length and density of the sample as a function of temperature. For the alkali halides there is some scarcity of data, to temperatures as low as 4.2°K, on such physical properties as linear-thermal-expansion coefficients, densities, and specific heats.

For the cases in which no experimental data on the linear-thermal-expansion coefficient and the density were available at low temperatures the length and densities of the samples were determined as follows. Grüneisen's[24] relation states that α/c_p is a constant independent of temperature where α is the linear-

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thermal-expansion coefficient and c_p is the specific heat at constant pressure. Once $\alpha(T)$ is known the length of the sample at a temperature, T, may be determined from the relation

$$L(T)=L_0\left[1-\int_{300}^{T}\alpha(T)dT\right], \tag{4}$$

where L_0 is the length of the sample at 300°K. For those cases in which low-temperature data for the density were not available it was computed as a function of temperature assuming a cube of side L_0 at 300°K and side $L(T)$ at temperature T°K. The density using this approach is given by

$$\rho(T)=\rho_0/[1-3\alpha(T)\Delta T], \tag{5}$$

where ρ_0 is the density at 300°K. In the few cases where experimental data on the linear thermal expansion coefficient and the density were available at low temperatures checks were made of this method of estimating $\alpha(T)$ and $\rho(T)$. The agreement was to within a few percent. For actual velocity calculations experimental values of $\alpha(T)$ and $\rho(T)$ were always used when available.

Table I lists the literature sources for the experimental values of the various physical quantities used in determining the elastic constants. In Table II the results obtained in this research are compared with other published values. The elastic constants of all the materials studied have been measured at room temperature by other investigators. The agreement in general is quite good and in the majority of cases is well within the estimated experimental error as can be seen from the percentage differences given in parentheses. In comparing data taken at "room temperature" it should be kept in mind that as much as a 10°C difference in temperature is possible. This could result in changes of the elastic constants by as much as 1% in some cases which is greater than many of the differences observed.

Despite the lack of data for the low-temperature thermal-expansion coefficient and the density, the primary source of error in the determination of the elastic constants is the measurement of the round-trip travel times in the specimens. The resulting estimated error in c_{11} and c_{44} is ±0.5%. The error in c_{12} is larger due to its being determined from the relatively small difference in two larger measured quantities. A conservative estimate would place it at ±5%. The agreement seen in Table II between the data of various investigators using different experimental methods indicates that it is less, of the order of 2 or 3%. The low-temperature data of Overton and Swim[8] and of Fugate and Schuele[7] is in good agreement with the present measurements with the exception of Overton and Swim's c_{12}. The 12% difference observed would seem to be outside our experimental error.

TABLE I. Literature sources for the various physical quantities used in determining the elastic constants as a function of temperature from the experimental velocities.

Material	Density	Expansion coefficient	Specific heat c_p	c_v	Lattice constant
LiCl	a			b	c
NaF	a f	d		e	c
NaCl	a f	g i	h	h j	c
NaBr	a f	d		e	c
KF	a		k		c
RbCl	a				c
RbBr	a	l	h	h	c
RbI	a	m	h	h	c

[a] *International Critical Tables* (McGraw-Hill Book Company, Inc., New York, 1928), Vol. 3.

[b] D. F. Moyer, J. Phys. Chem. Solids **26**, 1459 (1965).

[c] *International Critical Tables* (McGraw-Hill Book Company, Inc., New York, 1928), Vol. 1.

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[m] G. K. White, Proc. Roy. Soc. (London) **A286**, 204 (1965).

The elastic constants measured in this research are given in Tables III–VIII. The values shown for NaF, NaCl, NaBr, RbBr, and RbI were taken from smoothed curves of the data. Values are quoted only for the temperature ranges where measurements were actually made. A study of the temperature dependence of the constants for LiCl, KF, and RbCl was not made so only room temperature and 4.2°K data are given in Table VIII. The compressibility,

$$\beta=3/(c_{11}+2c_{12}) \tag{6}$$

computed from the values of c_{11} and c_{12} at 4.2°K is also given in Tables III–VIII. The observed values shown for comparison are the results of an extrapolation to 0°K of data taken at room temperature by Slater.[25] A possible error of as much as 20% is predicted by Slater for these extrapolated values.

Comparison of Experimental Elastic Constants with Theory

Several theoretical calculations of the elastic constants of the alkali halides at $T=0$°K have been made. Krishnan and Roy,[13] utilizing the Born-Mayer[18] model of lattice dynamics, calculated the constants of all the materials studied in this research. The Born-Mayer model contains only central, single-body forces and hence predicts $c_{12}=c_{44}$. Karo[14] used the 0°K values of the lattice constant and the compressibility to calculate the elastic constants of several alkali halides according

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TABLE II. Comparison of elastic constants with the published work of other investigators. The absolute value of the percentage difference between other published work and our results is given in parentheses. Data are at room temperature unless otherwise indicated.

Investigator	Material		Elastic constants in units of 10^{11} dyne/cm^2		
			c_{11}	c_{12}	c_{44}
	LiCl		4.927	2.31	2.495
Haussühl[a]			4.943 (0.3%)	2.28 (1.3%)	2.46 (1.4%)
	NaF		9.690	2.45	2.801
Haussühl[a]			9.70 (0.1%)	2.43 (0.8%)	2.81 (0.4%)
Miller and Smith[b]			9.700 (0.1%)	2.380 (2.9%)	2.822 (0.7%)
Bergmann[c]			9.70 (0.1%)	2.56 (4.5%)	2.80 (=)
	NaCl		4.899	1.309	1.270
		80°K	5.648	1.142	1.330
		4.2°K	5.733	1.123	1.331
Haussühl[a]			4.936 (0.8%)	1.29 (1.5%)	1.265 (0.4%)
Bergmann[c]			4.82 (1.6%)	1.27 (3%)	1.22 (4%)
Bhagavantam[d]			4.97 (1.4%)	1.27 (3%)	1.27 (=)
Galt[e]			4.87 (0.6%)	1.24 (5%)	1.26 (0.8%)
Huntington[f]			4.85 (1%)	1.23 (6%)	1.265 (0.4%)
Overton and Swim[g]			4.864 (0.7%)	1.258 (3.9%)	1.275 (0.4%)
		80°K	5.685 (0.7%)	0.986 (14%)	1.327 (0.2%)
	Extrapolated to 0°K		5.75 (0.3%)	0.986 (12%)	1.327 (0.2%)
Rose[h]			5.06 (3.2%)	1.30 (0.7%)	1.278 (0.6%)
		80°K	5.76 (2.2%)	1.17 (2%)	1.332 (≃)
Fugate and Schuele[i]		4.2°K	5.834 (1.8%)	1.192 (6%)	1.331 (≃)
	NaBr		4.000	1.00	1.002
Haussühl[a]			4.012 (0.3%)	1.09 (9%)	0.99 (1%)
Bhagavantam[j]			3.87 (3.3%)	0.97 (2.9%)	0.97 (3%)
Bergmann[c]			4.02 (0.5%)	1.11 (11%)	1.00 (≃)
	KF		6.490	1.52	1.232
Haussühl[a]			6.56 (1.1%)	1.46 (3.9%)	1.25 (1.5%)
	RbCl		3.646	0.647	0.468
Haussühl[a]			3.634 (0.3%)	0.615 (4.9%)	0.465 (0.6%)
	RbBr		3.135	0.512	0.3774
Haussühl[a]			3.157 (0.7%)	0.495 (3.4%)	0.38 (0.7%)
Bolef and Menes[k]			3.17 (1.1%)	0.42 (18%)	0.388 (2.7%)
Reinitz[l]			3.15 (0.5%)	0.493 (3.4%)	0.384 (2%)
	RbI		2.575	0.34	0.2778
Haussühl[a]			2.583 (0.3%)	0.37 (9%)	0.278 (0.1%)
Bolef and Menes[k]			2.56 (0.7%)	0.31 (9%)	0.287 (3.1%)
Reinitz[l]			2.54 (1.4%)	0.407 (20%)	0.276 (0.6%)

[a] Reference 10.
[b] R. A. Miller and C. S. Smith, J. Phys. Chem. Solids **25**, 1279 (1964).
[c] Reference 11.
[d] S. Bhagavantam, Proc. Roy. Soc. (London) **A187**, 381 (1946).
[e] Reference 6.
[f] Reference 22.
[g] Reference 8.
[h] Reference 9.
[i] Reference 7.
[j] S. Bhagavantam, Proc. Ind. Acad. Sci. **A41**, 72 (1955).
[k] D. I. Bolef and M. Menes, J. Appl. Phys. **31**, 1010 (1960).
[l] Reference 36.

TABLE III. Elastic constants of NaF.

Temperature °K	Density g/cc	c_{11}	c_{12}	c_{44}	β^{el}	β^{obs}
		10^{11} dyne/cm^2			10^{-12} cm^2/dyne	
300	2.796	9.630	2.459	2.794	2.062	···
290	2.799	9.690	2.452	2.801		
280	2.802	9.749	2.444	2.807		
270	2.805	9.807	2.436	2.813		
260	2.808	9.862	2.428	2.819		
250	2.811	9.921	···	···		
240	2.814	9.980	···	···		
230	2.816	10.04	···	···		
220	2.819	10.10	···	···		
210	2.822	10.16	···	···		
200	2.824	10.21	···	···		
190	2.827	10.27	···	···		
80	2.847	10.71	2.312	2.897		
4	2.851	10.85	2.290	2.899	1.944	···

TABLE IV. Elastic constants of NaCl.

Temperature °K	Density g/cc	c_{11}	c_{12}	c_{44}	β^{el}	β^{obs}
		10^{11} dyne/cm^2			10^{-12} cm^2/dyne	
300	2.162	4.870	1.311	1.266	4.004	4.20[a]
290	2.164	4.899	1.309	1.270		
280	2.166	4.927	1.308	1.275		
270	2.169	4.957	1.306	1.280		
260	2.171	4.985	1.305	1.285		
250	2.174	5.014	1.302	1.290		
240	2.176	5.045	1.299	1.295		
230	2.178	5.078	1.294	1.299		
220	2.181	5.114	···	···		
210	2.183	5.150	···	···		
200	2.185	5.190	···	···		
190	2.188	5.230	···	···		
80	2.212	5.648	1.142	1.330		
4	2.217	5.733	1.123	1.331	3.760	3.3[a]

[a] Slater, Ref. 25; β at 4°K extrapolated from room-temperature data.

Table V. Elastic constants of NaBr.

Temperature °K	Density g/cc	c_{11}	c_{12}	c_{44}	β^{el}	β^{obs}
		10^{11} dyne/cm^2			10^{-12} cm^2/dyne	
300	3.202	3.970	1.001	0.998	5.023	5.02[a]
290	3.206	4.000	1.000	1.002		
280	3.210	4.031	0.999	1.005		
270	3.214	4.062	0.998	1.008		
260	3.218	4.092	0.997	1.011		
250	3.221	4.122	0.996	1.014		
240	3.225	4.153	0.995	1.017		
230	3.229	4.184	···	···		
220	3.233	4.213	···	···		
210	3.237	4.244	···	···		
200	3.240	4.275	···	···		
80	3.286	4.645	0.988	1.060		
4	3.299	4.800	0.986	1.070	4.430	3.9[a]

[a] Slater, Ref. 25; β at 4°K extrapolated from room-temperature data.

to the Born-Mayer[26] model as used by Kellerman.[27] Mitskevich[16] has extended the above type of calculation by taking into account the dynamics of the crystalline lattice and has reported values for the elastic constants of NaCl. Löwdin[12] has presented a rather detailed quantum-mechanical calculation of the cohesive energy and the elastic constants of a solid. He used a many-body potential of central type and correctly predicted the failure of the Cauchy relation ($c_{12} \neq c_{44}$ for real materials). More recently Dick[15] introduced a modification of the Born-Mayer model which includes many-body forces arising from a consideration of the overlap of the electronic shells of the ions. His calculations are primarily concerned with the quantity $\Delta = c_{12} - c_{44}$ which expresses the degree of failure of the Cauchy relation.

The theoretical values of the elastic constants obtained by the above investigators are given in Table IX with the 4.2°K experimental data. The agreement between experiment and theory is in general fair with the best over-all agreement being with the work of Krishnan and Roy. Mitskevich's inclusion of the dynamics of the lattice into his calculation for NaCl does not result in a significant improvement of the agreement with experiment. Karo's use of the low-temperature lattice constant and compressibility also does not yield results which differ much from the work of Krishnan and Roy. Dick's results for c_{11} are in rather poor agreement with experiment even though his values for c_{12} and c_{44} are in reasonable agreement in most cases. This is partially to be expected since he was primarily interested in calculating Δ and not the absolute values of the elastic constants. Löwdin's quantum-mechanical calculation yields surprisingly good results considering the complexity of the problem. More will be said about the work of Löwdin and of

Table VI. Elastic constants of RbBr.

Temperature °K	Density g/cc	c_{11}	c_{12}	c_{44}	β^{el}	β^{obs}
		10^{11} dyne/cm^2			10^{-12} cm^2/dyne	
300	3.349	3.107	0.515	0.3760	7.25	7.94[a]
290	3.352	3.135	0.512	0.3774		
280	3.356	3.164				
270	3.359	3.191				
260	3.363	3.220				
250	3.366	3.249				
240	3.370	3.276				
230	3.373	3.305				
220	3.377	3.334				
210	3.380	3.361				
200	3.384	3.390				
190	3.387	3.418				
180	3.391	3.446				
170	3.394	3.474				
160	3.398	3.503				
150	3.401	3.530				
140	3.404	3.559				
80	3.424	3.725	0.474	0.4050		
70	3.426	3.751	0.474	0.4060		
60	3.428	3.775	0.474	0.4068		
50	3.430	3.799	0.474	0.4073		
40	3.432	3.820	0.474	0.4076		
30	3.433	3.839	0.474	0.4080		
20	3.434	3.853	0.474	0.4083		
10	3.434	3.860	0.474	0.4085		
4	3.434	3.863	0.474	0.4085	6.24	6.5[a]

[a] J. C. Slater, Ref. 25; β at 4°K extrapolated from room-temperature data.

Table VII. Elastic constants of RbI.

Temperature °K	Density g/cc	c_{11}	c_{12}	c_{44}	β^{el}	β^{obs}
		10^{11} dyne/cm^2			10^{-12} cm^2/dyne	
300	3.549	2.550	0.34	0.2773	9.30	9.58[b]
290	3.553	2.575	0.34	0.2778		
80	3.648	3.061		0.2890		
70	3.652	3.084		0.2895		
60	3.656	3.108		0.2901		
50	3.659	3.130		0.2906		
40	3.663	3.154		0.2911		
30	3.665	3.175		0.2915		
20	3.667	3.190		0.2918		
10	3.668	3.203		0.2920		
4	3.668	3.210	0.36[a]	0.2920	7.71	7.6[b]

[a] The value of c_{12} for RbI at 4°K is an extrapolation of the room-temperature value based on the temperature dependence of the velocity in a direction a few degrees off the [110] direction. Even though this velocity measurement yields an absolute value of c_{12} at room temperature which differs from that obtained from a velocity measurement in the [110] direction it is felt that the temperature dependences in the two cases should not differ very much.

[b] J. C. Slater, Ref. 25; β at 4°K extrapolated from room-temperature data.

Table VIII. Elastic constants of LiCl, KF, and RbCl at 295 and 4.2°K.

Material	Temperature °K	Density g/cc	c_{11}	c_{12}	c_{44}	β^{el}	β^{obs}
			10^{11} dyne/cm^2			10^{-12} cm^2/dyne	
LiCl	295	2.068	4.927	2.31	2.495	3.15	3.41[a]
	4.2	2.111	6.074	2.27	2.692	2.82	2.7[a]
KF	295	2.48	6.490	1.52	1.232	3.15	3.31[a]
	4.2	2.53	7.570	1.35	1.336	2.92	3.2[a]
RbCl	295	2.76	3.646	0.647	0.468	6.08	
	4.2	2.82	4.297	0.649	0.493	5.36	

[a] J. C. Slater, Ref. 25; β at 4°K extrapolated from room-temperature data.

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[26] M. Born, *Atomtheorie des festen Zustandes* (J. B. Teubner, Berlin, 1923); M. Born and M. Goeppert-Mayer, *Handbuch der Physik* (Springer-Verlag, Berlin, 1933), Vol. 24, Part 2.

[27] E. W. Kellerman, Trans. Roy. Soc. (London) **238**, 513 (1940); Proc. Roy. Soc. (London) **A178**, 17 (1941).

TABLE IX. Comparison of elastic constants measured at 4.2°K with theoretical calculations for $T=0$°K.

Source	Material	Elastic constants in units of 10^{11} dyne/cm^2 c_{11}	c_{12}	c_{44}
Experiment	LiCl	6.074	2.27	2.692
Krishnan and Roy[a]		5.5	1.8	1.8
Dick[b]		10.06	2.21	1.90
Karo[c]		5.59	1.89	1.89
Experiment	NaF	10.85	2.290	2.899
Krishnan and Roy[a]		8.5	2.8	2.8
Dick[b]		30.08	2.67	3.49
Löwdin[d]			2.52	3.16
Karo[c]		9.29	2.89	2.89
Experiment	NaCl	5.733	1.123	1.331
Krishnan and Roy[a]		5.0	1.3	1.3
Dick[b]		15.45	1.64	1.48
Löwdin[d]			1.119	1.484
Karo[c]		4.90	1.32	1.32
Mitskevich[e]		4.75	1.00	1.28
Experiment	NaBr	4.800	0.986	1.070
Krishnan and Roy[a]		4.3	1.0	1.0
Dick[b]		13.28	1.38	1.16
Karo[c]		4.28	1.05	1.05
Experiment	KF	7.570	1.35	1.336
Krishnan and Roy[a]		6.1	1.6	1.6
Dick[b]		18.68	0.868	2.05
Karo[c]		6.40	1.64	1.64
Experiment	RbCl	4.297	0.649	0.493
Krishnan and Roy[a]		3.6	0.7	0.7
Dick[b]		9.62	0.535	0.856
Karo[c]		3.38	0.72	0.72
Experiment	RbBr	3.863	0.474	0.4085
Krishnan and Roy[a]		3.2	0.6	0.6
Dick[b]		8.11	0.505	0.698
Karo[c]		2.88	0.60	0.60
Experiment	RbI	3.210	0.36	0.292
Krishnan and Roy[a]		2.8	0.4	0.4
Dick[b]		6.86	0.443	0.520
Karo[c]		2.52	0.46	0.46

[a] Reference 13. [c] Reference 14. [e] Reference 16.
[b] Reference 15. [d] Reference 12.

Dick in a later section concerning the failure of the Cauchy relation.

Temperature Dependence and Anisotropy

The temperature dependence of the elastic constants is an anharmonic effect and has been treated in various ways by several investigators. Born and co-workers[28–31] have studied the temperature dependence of the elastic constants for simple cubic lattices, using the so-called "quasiharmonic approximation" in which the eigenfrequencies of the lattice depend on the structure of the unit cell and hence the lattice constant. This method of calculation has been extended to low temperatures and nonprimitive lattices by Leibfried and Hahn.[32] Stern[33] has given a method for the direct calculation of the adiabatic elastic constants at any temperature. Leibfried and Ludwig[34] have given an extensive discussion of the problem of anharmonic effects in crystals in which they compare theory with experiment for the temperature dependence of several of the alkali halides. Also Nikanorov *et al.*[35] have presented a discussion of the temperature dependence of the elastic constants of the alkali halides with particular attention to the variation of the elastic anisotropy with temperature.

TABLE X. The elastic anisotropy factor, $A=2c_{44}/(c_{11}-c_{12})$ for the alkali halides at 300 and 4.2°K (the upper and lower lines for each halide refer to these temperatures, respectively).

	F	Cl	Br	I
Li	1.81[a] 1.57[a]	1.90 1.42		
Na	0.779 0.677	0.677 0.577	0.673 0.560	0.700[b] 0.536[b]
K	0.496 0.430	0.371[c] 0.309[c]	0.355[d] 0.29[d]	0.326[c] 0.233[c]
Rb		0.312 0.270	0.290 0.241	0.251 0.205

[a] Reference 3. [b] Reference 5. [c] Reference 4. [d] Reference 6.

Since the data discussed in the preceding articles does not differ significantly from our results we will not present a detailed discussion of the change with temperature of the elastic constants of the alkali halides studied in this work. We only mention that c_{11} is strongly temperature dependent while c_{12} and c_{44} depend very weakly on the temperature. Also c_{11} is of the order of five times larger than c_{12} and c_{44} in all cases. This general pattern of behavior has been pointed out by Leibfried and Ludwig.[34] A typical example of the temperature dependence of the elastic constants of the alkali halides is shown in Fig. 1 for the case of NaBr.

The anisotropy factor, $A=2c_{44}/(c_{11}-c_{12})$, which is equal to one for an isotropic material is given in Table X for 300 and 4.2°K. The anisotropy of the alkali halides at room temperature has been discussed by Reinitz.[36] He notes the large effect of the alkali ion on the magnitude of the anisotropy. Also he points out that the nature of the halide ion has more effect on the anisotropy as the size of the alkali ion increases. The data of Table X is in agreement with these observations. The fact that $\frac{1}{2}(c_{11}-c_{12})>c_{44}$ for all cases except

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[28] M. Born, J. Chem. Soc. **7**, 591 (1939).

[29] M. Born, Proc. Cambridge Phil. Soc. **39**, 100 (1943); M. Born and M. Bradburn, *ibid.* **39**, 104 (1943).

[30] M. Bradburn, Proc. Cambridge Phil. Soc. **39**, 113 (1943).

[31] M. Gow, Proc. Cambridge Phil. Soc. **40**, 151 (1944).

[32] G. Leibfried, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1955), Vol. 7, Part 1, pp. 104–324; G. Leibfried and H. Hahn, Z. Physik **150**, 497 (1958).

[33] E. A. Stern, Phys. Rev. **111**, 786 (1958).

[34] G. Leibfried and W. Ludwig, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1961), Vol. 12, pp. 275–444.

[35] S. P. Nikanorov and A. V. Stepanov, Fiz. Tver. Tela **6**, 1987 (1964) [English transl.: Soviet Phys.—Solid State **6**, 1569 (1965)]; S. P. Nikanorov, A. A. Nran'you, and A. V. Stepanov, Fiz. Tver. Tela **6**, 1996 (1964) [English transl.: Soviet Phys.—Solid State **6**, 1576 (1965)].

[36] K. Reinitz, Phys. Rev. **123**, 1615 (1961).

TABLE XI. The degree of failure of the Cauchy relation, $\Delta = c_{12} - c_{44}$ in units of 10^{11} dyne/cm^2, for the alkali halides at 300 and 4.2°K.

300°K ¦ 4.2°K Löwdin ¦ Dick	F		Cl		Br		I	
Li	−2.08[a]	−2.25[a]	−0.188	−0.422				
	−1.10	+0.326	−0.392	+0.309				
Na	−0.235	−0.609	+0.045	−0.208	+0.002	−0.090	+0.179[b]	+0.017[b]
	−0.644	−0.813	−0.365	+0.154		+0.225		+0.253
K	+0.291	+0.014	+0.041[c]	−0.123[c]	+0.08[d]	+0.04[d]	+0.086[c]	−0.148[c]
		−1.18	−0.112	−0.233		−0.118		−0.014
Rb			+0.180	+0.156	+0.135	+0.066	+0.062	+0.068
				−0.321		−0.193		−0.077

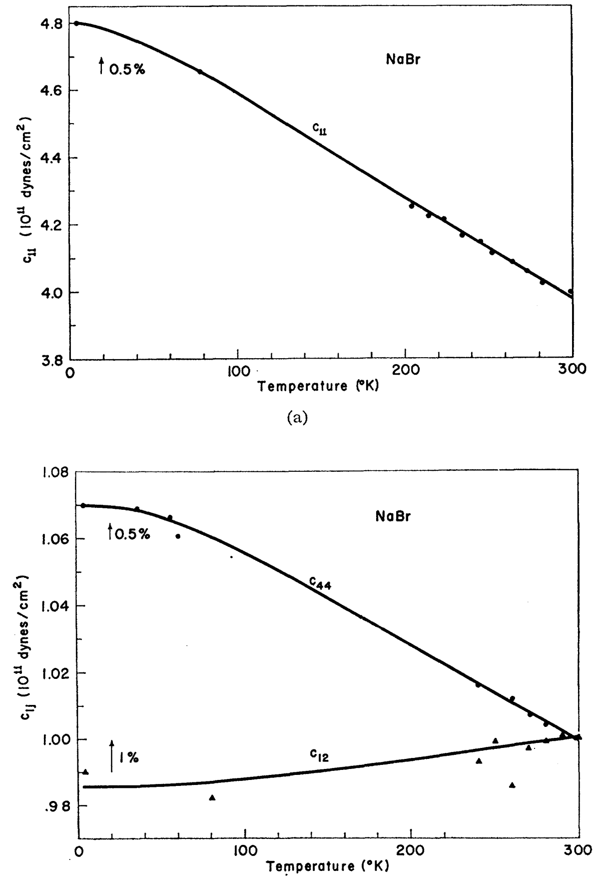
[a] Reference 3. [b] Reference 5. [c] Reference 4. [d] Reference 6.

the Li halides has been discussed by Huntington[37] as being due to the closed-shell repulsive potential between adjacent alkali and halide ions. Because of the small size of the Li$^+$ ion the most intimate contact is between the halide ions along the [110] directions and not the alkali and halide ions along the [100] directions. This results in a reversal in the sign of $\frac{1}{2}(c_{11} - c_{12}) - c_{44}$.

The temperature dependence of the anisotropy has been studied by Nikanorov *et al.*[35] They point out that for crystals of the NaCl type there is a sizable increase of A with temperature. As can be seen in Table X this results in the Na, K, and Rb halides becoming less isotropic at low temperatures while the Li halides become more isotropic as the temperature is decreased. According to Nikanorov *et al.*, the theory of Leibfried and Hahn[32] predicts that the anisotropy is only weakly temperature-dependent which is in disagreement with the experimental results.

Failure of the Cauchy Relation

The Cauchy relations, which for a cubic system reduce to $c_{12} = c_{44}$, are predicted to be true if the forces between the ions in a solid are of central, single-body character, the ions are centers of inversion symmetry, and the crystal is in an unstrained state. As can be seen in Table XI, $\Delta = c_{12} - c_{44}$ is not equal to zero for any of the materials studied. In fact Δ actually changes sign from 300 to 4.2°K for several of the alkali halides. For comparison with experiment the theoretical values of Δ given by Löwdin[12] and by Dick[15] are also shown in Table XI. For a more complete comparison with theory the experimental work of Briscoe and Squire[3]



(a)

(b)

FIG. 1. The elastic constants of NaBr as a function of temperature. The scatter in the data and the general features of the temperature dependence are typical of the alkali halides.

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[37] H. B. Huntington, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 7, pp. 213–351.

on LiF, Claytor and Marshall[5] on NaI, Norwood and Briscoe[4] on KCl and KI, and Galt[6] on KBr has been included in Table XI.

The most successful and the most basic attempt to account for the failure of the Cauchy relation in the alkali halides has been the work of Löwdin. As can be seen from Table XI Löwdin's theoretical values of Δ for LiF, LiCl, NaF, NaCl, and KCl (these are all the alkali halides for which he actually computed Δ) are in remarkable agreement with the 4.2°K experimental values of Δ. Dick's calculations of Δ are based on a modification of the Born-Mayer model in which he introduces exchange-charge interactions of a many-body character. The introduction of these exchange-charge interactions into the Born-Mayer model leads to a predicted Δ which is not zero. These interactions are a result of the overlap of the electron charge densities of the positive and the negative ions in the alkali halide crystals. According to Dick his calculations are expected to be the most reliable when the positive ion is small compared to the negative ion but not so small as to cause the negative ions to overlap. Thus his calculations should be poor for the lithium halides because of the overlap of the negative ions and for KF because of the large size of the positive ion relative to the negative ion. Table XII in which $\Delta_{\text{exp 4.2°K}}-\Delta_{\text{theory}}$ is given shows this to be true with Dick's results being in quite poor agreement with experiment for LiF, LiCl, and KF. The calculated values of Δ for the K and Rb halides should improve as one follows the sequence F, Cl, Br, and I, because of the increasing size of the negative ion relative to the positive ion. Table XII shows this expected improvement between theory and experiment for the Rb halides but not the K halides even though the agreement between experiment and theory is best for KCl, KBr, and KI. The Na halides best fit Dick's criteria and consequently should yield the best agreement between theory and experiment. According to Tables XI and XII this is not found to be true when comparison is made with the 4.2°K values of Δ. Table XII shows $\Delta_{\text{exp 4.2°K}}-\Delta_{\text{theory}}$ to be larger for the Na halides than it is for KCl, KBr, KI, and RbI. Dick's[15] good agreement between experiment and theory for the Na halides is probably due to his use of mostly room-temperature elastic-constant data to compute Δ_{exp}. Huntington[37] has pointed out that the failure of the Cauchy relation is more marked at low temperatures. The data given in Table XI show this to be the case for the Li and Na halides (NaI excepted) but not the Rb halides. For the K halides the failure of the Cauchy relation is more marked at 4.2°K for KCl and KI and less marked for KF and KBr. The value of Δ is seen to increase with temperature in all cases (RbI excepted) resulting in the above mentioned changes in the degree of failure of the Cauchy relation.

TABLE XII. Comparison between experiment and theory for $\Delta=c_{12}-c_{44}$ at 4.2°K. The quantity given is $\Delta_{\text{exp 4.2°K}}-\Delta_{\text{theory}}$ calculated from Table X in units of 10^{11} dyne/cm^2 (the upper and lower lines for each halide refer to the comparisons with Dick and Löwdin, respectively).

	F	Cl	Br	I
Li	−2.576 −1.15	−0.731 −0.030		
Na	+0.204 +0.035	−0.362 +0.157	−0.315	−0.236
K	+1.194	−0.110 −0.011	+0.158	−0.162
Rb		+0.477	+0.259	+0.145

Mitskevich[16] has calculated Δ at $T=0°\text{K}$ for NaCl only. He obtains a value for Δ of −0.33 which is in good agreement with the experimentally observed value of −0.208. It would be interesting to have additional results using his theory to see if this agreement continues for other alkali halides.

No comparison has been made with the theoretical work of Herpin[38] and of Lothe.[39] In his paper Dick has compared their results on the failure of the Cauchy relation with his calculations.

Lattice Resonance Frequency

The infrared dispersion frequency, ω_0, can be related to the high- and low-frequency dielectric constants, ϵ_∞ and ϵ_0, and the compressibility, β, see for example Born and Huang.[18] Szigeti[40] derived the following relationship for lattices of the NaCl type:

$$\omega_0^2=[(\epsilon_\infty+2)(6R_0)]/[(\epsilon_0+2)\bar{M}\beta], \tag{7}$$

where R_0 is the nearest-neighbor distance and $\bar{M}$ is the reduced mass. Odelevski[41] has modified this formula by taking into account the nearest-neighbor anion interactions. Additional generalizations of the Szigeti formula have been made by Dick and Overhauser[42] and by Hanlon and Lawson.[43] Lundqvist[44] proposed a modification of Eq. (7) based on a quantum-mechanical approach to the problem the result of which is the replacement of $1/\beta$ in Eq. (7) by $[c_{44}-c_{12}+1/\beta]$.

In Table XIII experimental observations of ω_0 are compared with values computed using the 4.2°K compressibility, calculated from the elastic constants, in the Szigeti relation, Eq. (7), and Lundqvist's modification of Eq. (7). The modification of the Szigeti relation due to Odelevski was not used to calculate ω_0 because of the uncertainty in evaluating the anion-anion interaction parameter. Also included in Table

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[38] A. Herpin, J. Phys. Radium 14, 611 (1953).

[39] J. Lothe, Arch. Math. Naturvidenskab. 55, 1 (1959).

[40] B. Szigeti, Proc. Roy. Soc. (London) A204, 51 (1950).

[41] B. I. Odelevski, Izvest. Akad. Nauk. SSSR Ser. Fiz. 14, 232 (1950).

[42] B. G. Dick, Jr. and A. W. Overhauser, Phys. Rev. 112, 90 (1958).

[43] J. E. Hanlon and A. W. Lawson, Phys. Rev. 113, 472 (1959).

[44] S. O. Lundqvist, Arkiv Fysik 9, 435 (1955); 12, 263 (1957).

Table XIII. Infrared lattice resonance frequency calculated from the 4.2°K elastic constants of the alkali halides.

			ω_0 in units of 10^{13} cycles/sec			
Material	ϵ_0[a]	$\epsilon_\infty = n^2$[b]	Szigeti[c]	Lundqvist[d]	Karo[e]	Observed
LiCl	11.95	2.70	4.35	4.46	4.43	3.84[f] (290°K)
NaF	5.10	1.79	4.66	5.01	4.12	4.74[g] (100°K)
NaCl	5.87	2.38	3.27	3.54	2.94	3.19[h] (100°K)
NaBr	6.38	2.69	2.72	2.95	2.53	2.55[i] (290°K)
KF	5.46	1.83	3.64	3.57	3.45	3.62[f] (290°K)
RbCl	4.92	2.19	2.31	2.21	2.03	2.39[i] (4.2°K)
RbBr	4.87	2.33	1.74	1.71	1.50	1.82[i] (4.2°K)
RbI	4.94	2.63	1.50	1.47	1.33	1.54[i] (4.2°K)

[a] Values of ϵ_0 taken from S. Haussühl, Z. Naturforsch. **12a**, 445 (1957).

[b] Values of ϵ_∞ taken from Jones *et al.*, Ref. 45, except the index of refraction from the *Handbook of Chemistry and Physics* (Chemical Rubber Publishing Company, Cleveland, Ohio) was used in calculating ϵ_∞ for LiCl and KF.

[c] Calculated using the Szigeti relation, Ref. 40, Eq. (7) in this text.

[d] Values of ω_0 calculated using the Lundqvist, Ref. 44, modification of Eq. (7) in this text.

[e] Karo, Ref. 14.

[f] C. M. Randall, R. M. Fuller, and D. J. Montgomery, Solid State Commun. **2**, 273 (1964).

[g] Taken from review article by D. H. Martin, in *Advances in Physics* (Taylor and Francis, Ltd., London, 1965), Vol. 14, p. 39.

[h] Marvin Hass, Phys. Rev. **119**, 633 (1960).

[i] Jones *et al.*, Ref. 45.

XIII are Karo's[14] calculated values of ω_0. The agreement theory and observation is reasonably good in all cases with the Szigeti relation yielding slightly better fits to the experimental ω_0's for a majority of the materials. Before a detailed comparison and discussion can be made of the various approaches, cited above, to relating ω_0, β, ϵ_∞, and ϵ_0 more data at low temperature is needed, see for example, Jones *et al.*[45]

Debye Temperature

The only contribution to the specific heat of dielectric crystals, such as the alkali halides, at low temperatures should be that due to the thermal vibrations of the lattice. Debye[17] and Born and von Kármán[46] have shown that at sufficiently low temperatures the specific heat at constant volume of face-centered cubic dielectric crystals can be represented by

$$c_v = 2(464.3)(T/\Theta_0^c)^3 \text{ cal/deg mole}, \qquad (8)$$

where T is the absolute temperature and Θ_0^c is a constant characteristic of the material. This constant is called the "Debye temperature."

If one assumes that low-energy thermal modes of vibration and long-wavelength mechanical modes of vibration are equivalent at low temperature then it is possible to calculate a limiting value, Θ_0^{el}, of the Debye temperature from measured low-temperature elastic constants. This procedure requires the calculation of the three sound-wave velocities (one longitudinal and two transverse) as a function of direction in the crystal and then the averaging of the reciprocal of each velocity cubed over all directions. Approximate methods for accomplishing this have been developed by Quimby and Sutton,[47] Houston,[48] Betts *et al.*,[49] and Anderson.[50] From a computer calculation de Launay[19,51] has prepared tables from which Θ_0^{el} may be derived.

We have used the procedures described by Betts *et al.*, and by Anderson and de Launay's tables to determine Θ_0^{el} from the elastic constants measured at 4.2°K. For the materials studied $[0.203 \leq A \leq 1.57$, where $A = 2c_{44}/(c_{11} - c_{12})]$ Betts *et al.*, state that Θ_0^{el}'s calculated using their procedure should be accurate to about 1%. In general we have found that de Launay's tables yield Θ_0^{el}'s that are larger than those calculated from Betts *et al.*, by approximately 1%. Alers and Neighbours[52] have determined Θ_0^{el} using a computer program in which the average velocity function was found at 120 points uniformly spread over the unit triangle for cubic symmetry. They obtain values of Θ_0^{el} for several alkali halides which differ from the results of de Launay's tables by less than 0.4%. Increasing the number of points considered in the unit triangle to 933 only changed their values of Θ_0^{el} by about 0.1%. This would indicate that de Launay's tables give the true value of Θ_0^{el} to within an error of less than 0.5%. The method described by Anderson produced values of Θ_0^{el} which differed by several percent from the results of de Launay's tables. In view of the preceding we quote in Table XIV only the values of Θ_0^{el} calculated from de Launay's tables and the previously reported results of Alers and Neighbours' numerical-integration calculation for LiF, NaCl, KCl, KBr, and KI. In addition to the eight alkali halides studied in this research we have included in Table XIV Θ_0^{el}'s obtained from the work of Briscoe and Squire[3] on LiF, Claytor and Marshall[5] on NaI, Norwood and Briscoe[4] on KCl and KI, and Galt[6] on KBr.

Other than from the method of calculation, uncertainty in Θ_0^{el} may be due to errors in the low-temperature elastic constants. Norwood and Briscoe using the procedure of Betts *et al.*, have calculated the error in Θ_0^{el} for KCl assuming the error in c_{11} to be $\pm 0.4\%$, in c_{44} to be $\pm 0.6\%$, and in c_{12} to be $\pm 10\%$. Considering all possible combinations of plus and minus errors they found that the values of Θ_0^{el} fell between 233.3 and 235.1°K. Thus the error in Θ_0^{el} for KCl due to the quoted errors in the elastic constants is only $\pm 0.4\%$. We have performed a similar analysis for RbI. Assuming the error in c_{11} and c_{44} to be $\pm 1\%$ and in c_{12} to be $\pm 5\%$ we find that all the values of Θ_0^{el} fall between 105.5 and 104.7°K which again is an error of $\pm 0.4\%$. The calculated value of Θ_0^{el} is more sensitive to changes

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[45] G. O. Jones, D. H. Martin, P. A. Mawer, and C. H. Perry, Proc. Roy. Soc. (London) **A261**, 10 (1961).

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[47] S. L. Quimby and P. M. Sutton, Phys. Rev. **91**, 1122 (1953); P. M. Sutton, Phys. Rev. **99**, 1826 (1955).

[48] W. V. Houston, Rev. Mod. Phys. **20**, 161 (1948).

[49] D. D. Betts, A. B. Bhatia, and M. Wyman, Phys. Rev. **104**, 37 (1956).

[50] O. L. Anderson, J. Phys. Chem. Solids **24**, 909 (1963).

[51] J. de Launay, J. Chem. Phys. **30**, 91 (1959).

[52] G. A. Alers and J. R. Neighbours, Rev. Mod. Phys. **31**, 675 (1959).

TABLE XIV. Debye temperatures at $T=0$°K of the alkali halides in °K.

	F		Cl		Br		I	
	Θ_0^{el}	Θ_0^c	Θ_0^{el}	Θ_0^c	Θ_0^{el}	Θ_0^c	Θ_0^{el}	Θ_0^c
Li	734.4±4[a] 734.1[e]	737±9[b] 722±6[f]	429±2.2[c]	422±6[d]				
Na	491.5±2.4[c]		321.2±1.6[c] 321.7[i] 321.9[e]	320.6±1.5[g]	224.6±1.2[c]		167.6±0.85[h] 167.9[j]	164.2±1[g] 164.3±1.5[k] 163.2±1[h]
K	335.9±1.7[c]		236.3±1.2[l] 237.1[e]	235.1±0.5[g] 233±3[m] 229±2[n]	172.8±0.85[e]	174.3±0.7[g] 173.8±1.5[k]	130.9±2[l] 131.5[e]	132.3±1[g] 133.1±1.5[k] 128.3[f]
Rb			168.9±0.85[c]	165[p]	136.5±0.7[c]	131[p]	108.0±0.55[c]	103[p]

[a] Briscoe and Squire, Ref. 3.
[b] Martin, Ref. 55.
[c] Present work.
[d] D. F. Moyer, J. Phys. Chem. Solids **26**, 1459 (1965).
[e] Θ_0^{el}'s calculated by Alers and Neighbours, Ref. 52 (120 point numerical integration scheme), using the low-temperature elastic-constant data of Briscoe and Squire (LiF), Ref. 3; Overton and Swim (NaCl), Ref. 8; Norwood and Briscoe (KCl and KI), Ref. 4; and Galt (KBr), Ref. 6.
[f] Scales, Ref. 56.
[g] Barron *et al.*, Ref. 53.
[h] Claytor and Marshall, Ref. 5.
[i] Calculated from data of Fugate and Schuele, Ref. 7, using de Launay's tables, Ref. 51.
[j] Recomputation of Θ_0^{el} for NaI by Martin, Ref. 54, using de Launay's tables, and the data of Claytor and Marshall, Ref. 5, with the thermal-expansion-coefficient data of G. K. White, Proc. Roy. Soc. (London) **A286**, 204 (1965).
[k] Martin, Ref. 54.
[l] Norwood and Briscoe, Ref. 4.
[m] P. H. Keesom and N. Pearlman, Phys. Rev. **91**, 1354 (1953).
[n] W. D. Seward and V. Narayanamurti, Phys. Rev. **148**, 463 (1966).
[p] C. T. Alexander and R. O. Pohl, Ref. 57, private communication of preliminary results.

in c_{44} and c_{11} than to changes in c_{12}. The above 1% changes in c_{11} and c_{44} for RbI resulted in 0.2% and 0.4% changes, respectively, in Θ_0^{el}. Changes of 5% and 10% in c_{12} for RbI only changed Θ_0^{el} by 0.05% and 0.1%, respectively. Using the 4.2°K elastic-constant data of Fugate and Schuele[7] for NaCl we have calculated Θ_0^{el} using de Launay's tables. The resulting Θ_0^{el} of 321.7°K differs from our value of 321.2°K for the Θ_0^{el} of NaCl by only 0.5°K which is a difference of 0.17%. Without going into a detailed error analysis for each alkali halide it seems reasonable, in view of the preceding discussion, to assume an error in Θ_0^{el}, for all materials studied, of ±0.5% due to errors in the elastic constants.

Specific-heat measurements have been made in the liquid-helium temperature range for the alkali halides listed in Table XIV with the exception of NaF, NaBr, and KF. In several cases different investigators have studied the same material at temperatures below 4.2°K. Barron *et al.*,[53] reported values of Θ_0^c for NaCl, NaI, KCl, KBr, and KI derived, using an extrapolation procedure, from specific-heat data taken in the 2.8 to 20°K temperature range. These investigators plotted c_v/T^3 against T^2 and obtained Θ_0^c from the $T^2=0$ intercept of a line fitted to the data. Martin[54] has measured the specific heat of NaI, KBr, and KI at temperatures as low as 0.5°K. He has derived values of Θ_0^c assuming that the Debye temperature is a constant below 1.5°K and that all errors in the measurements are random. Martin[55] and Scales[56] have reported low-temperature specific-heat data for LiF and Scales[56] has given a value for the Θ_0^c of KI. Claytor and Marshall[5] performed specific-heat as well as elastic-constant measurements on NaI below 4.2°K. We are indebted to Alexander and Pohl[57] of Cornell University for their preliminary results on the low-temperature specific heat of RbCl, RbBr, and RbI. The errors quoted in Table XIV for Θ_0^c are those given by the various investigators. Alexander and Pohl give no estimate of the accuracy of their preliminary data.

As can be seen from Table XIV Θ_0^c and Θ_0^{el} are equal to within experimental error in almost all cases. An exception is NaI for which, as discussed earlier by Claytor and Marshall,[5] Θ_0^{el} is larger than Θ_0^c by approximately 2%. This is well outside the quoted limits of experimental error. Also for RbCl, RbBr, and RbI Θ_0^{el} is greater than Θ_0^c by 2 to 4%. How ever, the Θ_0^c's of Alexander and Pohl for the Rb halides are preliminary and final results are necessary in order to determine if this difference in Θ_0^{el} and Θ_0^c is real.

It has been suggested by Ludwig[58] that the inclusion of anharmonicity in the theory of lattice vibrations results in Θ_0^{el} not being equal to Θ_0^c. Leibfried and Ludwig,[34] from approximate calculations of particular models, estimate that Θ_0^{el} should be greater than Θ_0^c by 1 to 2%. In a subsequent article Barron and Klein[59] cite an error in Leibfried and

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[53] T. H. K. Barron, W. T. Berg, and J. A. Morrison, Proc. Roy. Soc. (London) **A242**, 478 (1957).
[54] D. L. Martin, Proc. Phys. Soc. (London) **83**, 99 (1964).
[55] D. L. Martin, Phil. Mag. **46**, 751 (1955).
[56] W. W. Scales, Phys. Rev. **112**, 49 (1958).
[57] C. T. Alexander and R. O. Pohl (private communication).
[58] W. Ludwig, J. Phys. Chem. Solids **4**, 283 (1958).
[59] T. H. K. Barron and M. L. Klein, Phys. Rev. **127**, 1997 (1962).

Ludwig's linear-chain calculation which had been cited as a calculable model for which $\Theta_0^{\mathrm{el}} \neq \Theta_0^{c}$. Furthermore Barron and Klein conclude that "since the general theory implies that $\Theta_0^{c} = \Theta_0^{\mathrm{el}}$, any differences found between them in theoretical calculations must be due to approximations in their explicit evaluation." The results of a calculation by Feldman[60] of first-order quantum corrections to the elastic frequencies (zero-point energy) and to the specific heat (vibrational anharmonicity) of a Bravais crystal near $T = 0$°K supports the conclusion of Barron and Klein. Feldman shows explicitly that these corrections maintain the equality of Θ_0^{el} and Θ_0^{c} to the same order in an appropriate ordering parameter. Nevertheless it is interesting to look at the differences in Θ_0^{el} and Θ_0^{c} taken from Table XIV even though they are within the limits of experimental error in the majority of cases. Excluding LiF, for which there is disagreement concerning the specific-heat data, there are only two materials, KBr and KI, for which $\Theta_0^{\mathrm{el}} < \Theta_0^{c}$. In seven cases, if one includes the Rb halides, $\Theta_0^{\mathrm{el}} > \Theta_0^{c}$. While this apparent trend may be nothing more than a statistical fluctuation or the result of some systematic error in the experiments, it is quite suggestive, particularly if the preliminary results of Alexander and Pohl for the specific heat of the Rb halides are substantially correct. It should be noted that the previously discussed numerical-integration procedure of Alers and Neighbours[52] yielded Θ_0^{el}'s which are slightly larger than the results of de Launay's tables, see Table XIV, for the alkali halides in which $A < 1$, e.g., NaCl, KCl, and KI. LiF, for which $A > 1$ is the opposite of this but the values differ by only -0.04%. For NaCl, KCl, and KI the Θ_0^{el}'s differ by $+0.3$ to $+0.4\%$. Thus a more accurate numerical calculation of Θ_0^{el}, such as performed by Alers and Neighbours, would, if anything, probably only have the effect of increasing the above noted trend.

A striking equality of the Debye temperatures is noted if one examines the diagonal blocks of Table XIV, e.g., RbCl, KBr, and NaI for which the Debye temperatures are approximately 169, 173, and 168°K, respectively. Also note: RbBr (137°K) and KI (131°K), KCl (236°K) and NaBr (225°K), KF (336°K) and NaCl (321°K), and NaF (492°K) and LiCl (429°K). This approximate equality does not appear to be simply related to the average mass or size of the ions.

SUMMARY AND CONCLUSIONS

The importance of the alkali ion in determining the elastic properties of the alkali halides can be seen from an examination of the data. Reinitz[36] has already discussed this role of the metal ion in determining the room-temperature elastic constants and the elastic anisotropy factor, $A = 2c_{44}/(c_{11} - c_{12})$. The trends he notes are essentially the same at 4.2°K with the anisotropy constant being particularly dependent on the nature of the alkali ion. Also it is observed that the effect of the halide ion on the anisotropy is more pronounced as the size of the alkali ion increases, i.e., in going from the Li to the Rb halides. A considerable increase in A with temperature is observed. This results in the Li halides, for which $A > 1$, becoming less anisotropic as the temperature approaches absolute zero. However, the Na, K, and Rb halides, for which $A < 1$, become more anisotropic as the temperature decreases.

The Cauchy relation, $c_{12} = c_{44}$, is not satisfied at 4.2°K for any of the alkali halides. The degree of failure of the Cauchy relation, $\Delta = c_{12} - c_{44}$, is observed to increase with temperature. This results in the absolute value of Δ being larger at 4.2°K than at room temperature for the Li and Na halides (NaI excepted), and smaller for the Rb halides. Furthermore it is observed that the Cauchy relation is best satisfied at 4.2°K for the heavier halides, i.e., Br and I, of Na, K, and Rb. Of considerable note is the remarkable success of Löwdin's[12] quantum-mechanical calculation of the failure of the Cauchy relation in which he predicts reasonable magnitudes and the correct sign of Δ for LiF, LiCl, NaF, NaCl, and KCl. These are the only alkali halides for which Löwdin made numerical calculations.

A detailed and critical discussion of the various proposed relations between ω_0, β, ϵ_∞, and ϵ_0 is not possible until all four quantities are experimentally determined at 4.2°K. For the alkali halides all that is needed is more low-temperature data for ω_0, ϵ_∞, and ϵ_0. Such information would be of considerable value in elucidating the role of anharmonicity in the lattice dynamics of the alkali halides.

The Debye temperatures Θ_0^{el} and Θ_0^{c} are seen to agree within experimental error with the exception of NaI, RbCl, RbBr, and RbI. Nevertheless there is indication of a trend toward $\Theta_0^{\mathrm{el}} > \Theta_0^{c}$ as suggested by Ludwig.[58] Final results on the specific heats of RbCl, RbBr, and RbI should help considerably in determining if this suggested trend is real or the result of some systematic error in the experiments or analysis.

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