

Elastic Constants of Potassium Iodide and Potassium Chloride*

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The sound velocities and elastic constants have been measured for pure single crystals of KI and KCl by the ultrasonic pulse technique over the temperature range from 4°K to 300°K. In KI, $c_{11}=3.38$, $c_{12}=0.22$, and $c_{44}=0.368$ in units of 10^{11} dynes/cm² at 0°K according to our extrapolations from 80°K. In KCl, measurements of all three constants were made over the entire temperature range down to 4°K and their values at 0°K are $c_{11}=4.83$, $c_{12}=0.54$, and $c_{44}=0.663$ in units of 10^{11} dynes/cm². The Debye characteristic temperature at 0°K, θ_0 , has been calculated from these very low-temperature values of the elastic constants to give $129^\circ\pm 2^\circ\text{K}$ for KI and $234^\circ\pm 1^\circ\text{K}$ for KCl. The specific heats of KI, KCl, and KBr have been calculated in this paper by using a combination of a Debye and an Einstein term in the expression for the specific heat. These calculations indicate that the agreement between such a simple theory and experiment becomes better as the ratio of ionic radii and masses increases in these three salts. We point out that in the four alkali halides thus far studied in this laboratory, there is evidence that the Cauchy relation, $c_{12}=c_{44}$, is satisfied at about $T=\theta_0$. No reason is offered for this coincidence.

INTRODUCTION

THIS work has been done as part of a continuing program at The Rice Institute for furnishing more fundamental information on the temperature dependence of the elastic constants of alkali halides. The following paper reports work on the specific heats of two of these crystals by Scales.¹ A comparison can be made of the value of the characteristic temperature (θ_0) obtained from low-temperature specific heat measurements with that obtained from the data reported here near the absolute zero. In this way we may check on the methods²⁻⁴ of averaging the sound velocity over different directions in the crystal in order to calculate θ_0 . We are also interested in the theory of the frequency spectrum of lattice oscillations in order to give a better representation of the specific heat of these materials. We attempt to do this by considering the smaller ion in the lattice to behave somewhat like an independent Einstein oscillator while the larger ion behaves as a Debye continuum of standing waves. We shall show that such a theory agrees with experiment as the ratio of ionic radii and masses increases.

EXPERIMENTAL

The experimental apparatus used in this experiment is for the most part the same as was used by Overton and Swim,⁵ and Briscoe and Squire,⁶ for similar measurements in this laboratory. The echo-ranging technique was used to measure velocities of longitudinal and transverse waves along various directions in the single-crystal specimens. Because of the differential

contraction between the quartz transducer, the binder, and the specimen, very slow rates of cooling were necessary in order to minimize the chance of cleavage in the specimen. Generally, we cooled from room temperature to liquid air temperature in about 24 hours and in the case of KI the crystal developed cracks on all but one occasion as helium was transferred into the Dewar. As a result of this, actual measurements were made only for the longitudinal velocity in the [100] direction at helium temperature for KI. The binders used on KI were Dow Corning silicones XC-270 and C-271.

During the experiments on KCl, we decided to try to find a binder which would not solidify until a temperature was reached where the expansion coefficient of the specimen had decreased appreciably from its room temperature value. For KI and KCl, this does not occur until about 60°K. The successful binder tried was the natural gas from the wall outlet. During the cooling to liquid air temperature the specimen was not in contact with the quartz transducer. At liquid air temperature a bent glass tube was rotated so that its tip was above the center of the specimen. Natural gas was passed through a dry ice and acetone trap to remove water vapor. The flow was regulated such that liquefaction took place near the tip of the glass tube. After a few drops of liquid were deposited on the specimen, the tube was rotated out of the way and the transducer lowered until contact was made. In the case of X-cut quartz crystals, measurements could be made immediately. In using Y-cut crystals, the appearance of echos indicated that the natural gas did not firmly solidify until about 45°K. This behavior perhaps can be explained by the fact that the gas is a mixture of about 94% methane, 5% ethane, and the rest other light hydrocarbons. Echos obtained with this binder at 4°K were surprisingly good.

Using this binder, the transverse and longitudinal velocities in the [100] direction were obtained quite

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¹ W. W. Scales, following paper [Phys. Rev. **112**, 49 (1958)].² W. V. Houston, Revs. Modern Phys. **20**, 161 (1948).³ Betts, Bhatia, and Wyman, Phys. Rev. **104**, 37 (1956).⁴ J. DeLaunay, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1956), Vol. 2.⁵ W. C. Overton, Jr., and R. T. Swim, Phys. Rev. **84**, 758 (1951).⁶ C. V. Briscoe and C. F. Squire, Phys. Rev. **106**, 1175 (1957).

TABLE I. Elastic constants of KI in units of 10^{11} dynes/cm².

T	c_{11}	c_{12}	c_{44}
4.2	$3.38 \pm 2\%$	$0.22 \pm 30\%$	$0.368 \pm 2\%$
20	3.36	0.24	0.368
40	3.32	0.26	0.368
60	3.28	0.28	0.369
80	$3.23 \pm 1\%$	$0.30 \pm 15\%$	$0.369 \pm 1\%$
100	3.19	0.32	0.369
120	3.14	0.33	0.369
140	3.10	0.35	0.369
160	3.05	0.37	0.368
180	3.01	0.38	0.368
200	2.96	0.39	0.368
220	2.92	0.39	0.367
240	2.87	0.41	0.367
260	2.82	0.42	0.366
280	2.76	0.44	0.365
300	$2.71 \pm 1\%$	$0.45 \pm 9\%$	$0.364 \pm 1\%$

accurately at helium temperature. The constant c_{12} can be determined by measuring the velocity of a longitudinal wave in the $[110]$ direction and of a transverse wave in the $[110]$ direction with polarization perpendicular to the z axis. In the case of the polarized transverse wave, measurements were made at helium temperature but the echos were poor. Thus the value of c_{12} obtained from this measurement is subject to a sizeable error. In the case of the longitudinal wave, the specimen was cooled too rapidly during the helium transfer and the specimen cracked. The data from 90°K were extrapolated, however, giving two independent estimates of c_{12} at very low temperature. These values will be mentioned later in regard to errors in c_{12} .

The equations from which the constants are calculated from the measured velocities are given in books on solid state physics.^{4,7}

RESULTS

The elastic constants for KI and KCl are listed in Tables I and II. For KCl, the measurements of Durand,⁸

TABLE II. Elastic constants of KCl in units of 10^{11} dynes/cm².

T	Present work			Durand		
	c_{11}	c_{12}	c_{44}	c_{11}	c_{12}	c_{44}
4.2	4.832	0.54	0.663			
20	4.811	0.54	0.661			
40	4.780	0.55	0.660			
60	4.743	0.55	0.658			
80	4.697	0.55	0.657	4.81	0.6	0.664
100	4.644	0.57	0.655		0.6	
120	4.582	0.58	0.652		0.6	
140	4.510	0.59	0.650	4.62	0.6	0.658
160	4.453	0.59	0.648	4.55	0.6	0.655
180	4.394	0.60	0.646	4.48	0.6	0.651
200	4.331	0.61	0.643	4.40	0.6	0.648
220	4.274	0.62	0.640	4.33	0.6	0.645
240	4.218	0.62	0.638	4.24	0.6	0.641
260	4.158	0.63	0.635	4.16	0.6	0.637
280	4.095	0.65	0.632	4.08	0.6	0.634
300	4.032	0.66	0.629			

⁷ Charles Kittel, *Introduction to Solid State Physics* (John Wiley and Sons, Inc., New York, 1954).

⁸ M. A. Durand, *Phys. Rev.* **50**, 449 (1936).

by an earlier technique known as the composite oscillator, are listed for comparison. In Table I, the estimated maximum errors are listed with the numbers. For KCl, the room temperature maximum errors for c_{11} and c_{44} are $\pm 0.3\%$ and $\pm 0.5\%$. At 4°K we estimate the maximum errors to be $\pm 0.4\%$ and $\pm 0.6\%$. Since c_{12} must be determined by taking a difference between large numbers close together in value, an analysis of the propagation of errors shows that the percentage error in c_{12} can be large. For KCl, our analysis indicates a possible, but not probable, error of 35%. The effect of this error on the calculation of θ_0 will be discussed in more detail. The second estimate of c_{12} by using a transverse polarized wave in the $[110]$ direction indicates a value of c_{12} at 4°K equal to 0.60. The two values are about 9% apart, indicating that the error is not nearly as large as 35%.

Table III shows a comparison between room temperature values of the elastic constants of KI done in the present work and that done by static methods in 1929 by Bridgman.⁹ Table III also shows a comparison between our constants at 4°K and the theoretical

TABLE III. Values of elastic constants in units of 10^{11} dynes/cm² and compressibilities in units of 10^{-12} cm²/dyne of KI at room temperature and at low temperatures by various investigators.

	Present work $T \approx 300^\circ\text{K}$	Bridgman $T \approx 300^\circ\text{K}$	Present work $T = 4^\circ\text{K}$	Krishnan and Roy $T = 0^\circ\text{K}$	Slater ^a $T \approx 300^\circ\text{K}$
c_{11}	2.71	2.66	3.38	3.1	
c_{12}	0.45	0.425	0.22	0.5	
c_{44}	0.364	0.412	0.368	0.5	
β	8.33				8.54

^a J. C. Slater, *Proc. Am. Acad. Arts Sci.* **61**, 135 (1926).

calculations of Krishnan and Roy¹⁰ at absolute zero using a central force model.

Table IV shows a comparison of our values of elastic constants and compressibility for KCl at 4°K with the theoretical calculations of Krishnan and Roy,¹⁰ and Löwdin.¹¹ Also, the recent room temperature measurements of Eros and Reitz¹² are included for comparison.

The values of θ_0 have been calculated for each of the crystals by using DeLaunay's tables¹³ and by the formulas in the extension of Houston's work² by Betts, Bhatia, and Wyman.³ Table V shows these values compared with specific heat work of Berg and Morrison,¹⁴ and Scales.¹ From these results it becomes apparent that specific heat data and elastic constant

⁹ P. W. Bridgman, *Proc. Am. Acad. Arts Sci.* **64**, 19 (1929).

¹⁰ K. S. Krishnan and S. K. Roy, *Proc. Roy. Soc. (London)* **A210**, 481 (1952).

¹¹ Per Olov Löwdin, in *Advances in Physics*, edited by N. F. Mott (Taylor and Francis Ltd., London, 1956), Vol. 5, No. 17.

¹² S. Eros and J. R. Reitz, *J. Appl. Phys.* **29**, 683 (1958).

¹³ J. DeLaunay, extended tables; these were obtained from Dr. DeLaunay at Naval Research Laboratory, Washington D. C.

¹⁴ W. T. Berg and J. A. Morrison, *Proc. Roy. Soc. (London)* **A242**, 467 (1957).

data lead to values of θ_0 in good agreement with each other.

In order to obtain an idea of the error in θ_0 due to errors in the elastic constants, we programmed the computation of θ_0 according to the relations derived by Betts, Bhatia, and Wyman for the IBM-650 computer. We assumed the errors for c_{11} and c_{44} given previously and for c_{12} we assumed errors of 1, 10, and 35%. For each error in c_{12} we calculated the eight values of θ_0 obtained by taking all combinations of plus and minus errors. Each time we also calculated the eight θ 's listed in Betts, Bhatia, and Wyman's paper. We show the results for θ_8 only since it is assumed to be the best approximation. The results of this error analysis show, as does an examination of DeLaunay's tables, that the calculation is extremely insensitive to errors in c_{12} . Even with the 35% assumed error in c_{12} , all values fell between 232.5 and 235.8°K. For 10% error all values fell between 233.3 and 235.1°K. As a result of this analysis on KCl and a less extended one on KI, we conclude that the respective errors in θ_0 due to experimental errors in the constants are $\pm 1^\circ\text{K}$ and $\pm 2^\circ\text{K}$.

TABLE IV. Values of elastic constants in units of 10^{11} dynes/cm² and compressibilities in units of 10^{-12} cm²/dyne of KCl at room temperature and at low temperatures by various investigators.

	Present work $T \approx 300^\circ\text{K}$	Eros and Reitz $T \approx 300^\circ\text{K}$	Present work $T = 4^\circ\text{K}$	Löwdin $T = 0^\circ\text{K}$	Krishnan and Roy $T = 0^\circ\text{K}$
c_{11}	4.032	4.035	4.832		3.9
c_{12}	0.66	0.651	0.54	0.777	0.8
c_{44}	0.629	0.633	0.663	0.909	0.8
β			5.60	6.0	

DISCUSSION

The history of early attempts by Einstein and by Debye to describe theoretically the specific heats of materials is well known and will not be discussed here in detail. It suffices to say that only a detailed knowledge of the lattice vibration spectrum can lead to the correct theoretical values of the specific heat.

Briscoe and Squire⁶ have applied a rather simple technique in trying to improve the fit of a theoretical specific heat to experimental data on LiF. For a crystal such as LiF, where one ion is considerably larger than the other, they assume that the smaller ions are partly shielded from one another by the electron clouds of the larger, and that the smaller ions tend to act like independent Einstein oscillators. They compute the specific heat as a combination of an Einstein and a Debye function:

$$c_v = 3RF_D(\theta_0'/T) + 3RF_E(\theta_E/T).$$

The θ_E used comes from the restrahlen frequency or frequency of maximum infrared reflection. The θ_0' shown is not the usual θ_0 but $\theta_0/(2)^{1/2}$ since the larger ion is now considered to occupy the whole volume. We

TABLE V. Values of θ_0 in °K from elastic-constant work and specific heats at low temperatures.

	Elastic constant	Specific heat
KI		
DeLaunay's tables	131	
Betts, Bhatia, and Wyman	129±2	
Berg and Morrison		132.3
Scales		128
Krishnan and Roy (theoretical)	140	
KCl		
DeLaunay's tables	236	
Betts, Bhatia, and Wyman	234±1	
Berg and Morrison		235.1
Durand (extrapolated)	238	

emphasize that the theory contains no "adjustable parameters." It is worth noting that this manipulation gives back the correct specific heat at low temperatures.

As T goes to 0, one finds that $F_E(\theta_E/T) \ll F_D(\theta_0'/T)$, and

$$c_v = 3RF_D(\theta_0'/T) = 3R(4\pi^4/5)(T/\theta_0')^3 \\ = 6R(4\pi^4/5)(T/\theta_0)^3.$$

By means of this scheme, specific heats of KI, KCl, and KBr were calculated, the data of Galt¹⁵ on KBr being used. The results are shown in Figs. 1, 2, and 3. It is seen that the fit becomes increasingly better as the ratio of the ionic radii and masses increase in going from Cl to Br and to I. For KI this simple fit is quite good and indicates that the method may throw a little light on the true frequency spectrum of ionic cubic crystals where one ion is somewhat larger than the other. In no case is the Debye fit adequate.

One point of interest arising from this work is that the temperature where the Cauchy relation, $c_{12} = c_{44}$, is satisfied for alkali halide crystals whose constants

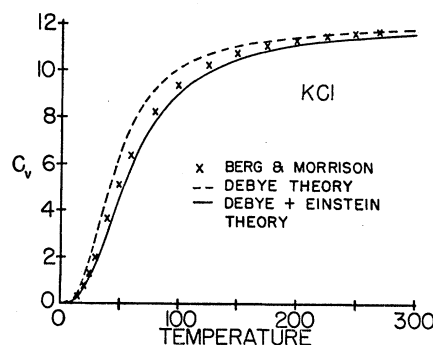


FIG. 1. Specific heat of potassium chloride in units of calories/mole °K versus temperature in °K. The crosses are experimental data. The broken line is calculated from the Debye theory ($\theta_0 = 235^\circ\text{K}$). The solid line represents a combination of the Debye and Einstein theories ($\theta_0' = 187^\circ\text{K}$). The Einstein characteristic temperature ($\theta_E = 227^\circ\text{K}$) is obtained from the restrahlen frequency shown in reference 7, p. 114.

¹⁵ J. K. Galt, Phys. Rev. 73, 1460 (1948).

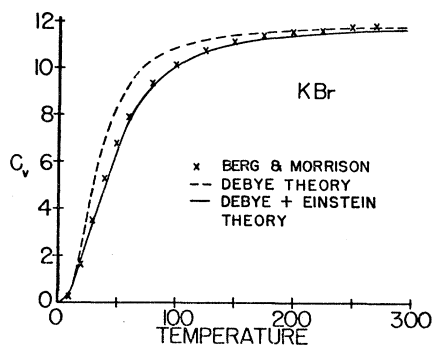


FIG. 2. Specific heat of potassium bromide in units of calories/mole $^{\circ}\text{K}$ versus temperature in $^{\circ}\text{K}$. The crosses are experimental data. The broken line is calculated from the Debye theory ($\theta_0=174^{\circ}\text{K}$). The solid line represents a combination of the Debye and Einstein theories ($\theta_0'=138^{\circ}\text{K}$). The Einstein characteristic temperature ($\theta_E=174^{\circ}\text{K}$) is obtained from the restrahlen frequency shown in reference 7, p. 114.

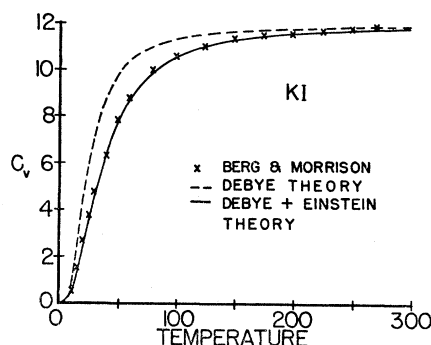


FIG. 3. Specific heat of potassium iodide in units of calories/mole $^{\circ}\text{K}$ versus temperature in $^{\circ}\text{K}$. The crosses are experimental data. The broken line is calculated from the Debye theory ($\theta_0=130^{\circ}\text{K}$). The solid line represents a combination of the Debye and Einstein theories ($\theta_0'=103^{\circ}\text{K}$). The Einstein characteristic temperature ($\theta_E=153^{\circ}\text{K}$) is obtained from the restrahlen frequency shown in reference 7, p. 114.

have been measured is at $T \cong \theta_0$. A summary of available data follows:

Substance	Temperature where $c_{12} = c_{44}$	θ_0	Investigator
KCl	265 $^{\circ}\text{K}$	235 $^{\circ}\text{K}$	Present work
KI	164 $^{\circ}\text{K}$	130 $^{\circ}\text{K}$	Present work
NaCl	300 $^{\circ}\text{K}$	322 $^{\circ}\text{K}$	Overton and Swim
LiF	well above 500 $^{\circ}\text{K}$	735 $^{\circ}\text{K}$	Briscoe and Squire

It is realized that there is considerable error involved in locating this point, but the tendency for the Cauchy relation to be satisfied in this manner does seem to exist. The data of Galt¹⁵ on KBr do not show the constants equal for any temperature, but they are close together in value everywhere so that the usual error in c_{12} might account for this.

In regard to agreement between elastic constant methods and specific heat methods of obtaining the Debye characteristic temperature at absolute zero, it should be pointed out that very recent work by Ludwig¹⁶

using anharmonic terms in the atomic potentials indicates that one should not necessarily expect the two to be exactly the same in alkali halides, even at absolute zero. In his model for krypton, he shows that one expects a difference between the measured values of the order of 2%, and that for alkali halides the difference should be about half of this figure. In the case of KI and KCl, it would be difficult to try to see differences of this sort because of experimental errors involved in each technique. In the case of KI, however, it is observed that the two estimates of θ_0 , made at the Rice Institute, differ by about 1 part in 130 and that the specific heat estimate was lower as Ludwig indicates.

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¹⁶ Wolfgang J. Ludwig, J. Phys. Chem. Solids 4, 283 (1958).