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Elastic Constants of CsBr, CsI, RbBr, and RbI†

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The elastic constants of two body-centered halides, CsBr and CsI, were determined as a function of temperature from 300°K to 73°K. The velocity measurements were obtained with an ultrasonic interferometer constructed according to the design principles of Williams and Lamb. Room temperature constants of RbBr and RbI samples were also measured. The values of C_{11}, C_{12}, and C_{44} in units of 10^{11} d/cm^2 at 22°C for these salts are given in the following table:

	C_{11}	C_{12}	C_{44}
CsBr	3.097	0.903	0.7500
CsI	2.434	0.636	0.6316
RbBr	3.15	0.493	0.384
RbI	2.54	0.407	0.276

The temperature dependence of all the cesium salt constants was negative and nearly linear over the temperature range investigated. It was found that with decreasing temperatures C_{44} increased more rapidly than C_{12} for the two cesium salts examined.

The elastic constant data of the sodium chloride type halides, compiled from the literature, are compared with those of the cesium chloride type salts.

INTRODUCTION

ELASTIC constants and their temperature dependence correlated with other physical measurements provide a valuable insight into the nature of atomic binding forces in solids.

For this reason the elastic constants of several materials, especially of the alkali halides, were extensively investigated by a variety of different methods. In 1929, using static methods, Bridgman[1] determined the stiffness constants of NaCl and LiF. Later Bergmann,[2] Durand,[3] Rose,[4] and Hunter and Siegel[5] measured the constants of LiF, NaCl, KBr, and KI. Huntington[6] used the ultrasonic pulse echo technique to obtain the elastic constants of LiF, NaCl, KBr, and KI. Galt[7] used the same method to obtain the temperature dependence of KBr constants. In 1949 the constants of NaCl were again measured as a function of pressure by Lazarus,[8] while the temperature dependence of NaCl was first obtained by this method by Overton and Swim[9] in 1951. Norwood and Briscoe[10] and Briscoe and Squire[11] determined the temperature dependence of elastic moduli of KCl, KI, and LiF, respectively. The moduli of NaI were evaluated by Haussuhl[12] and by Eros and Reitz.[13] Bhagavantam[14] used the ultrasonic wedge method to find the constants of NaBr. Employing his ultrasonic elastogram method, Bergmann[15] found the room temperature moduli of LiF, NaF, NaCl, NaBr, KCl, KBr, KI, RbCl, and RbI. Spangenberg and Haussuhl,[16] also by the Bergmann-Schaefer method, found the room temperature elastic constants for all the sodium chloride type alkali halides. The room temperature constants of CsBr were measured by Bolef and Menes,[17] while the temperature dependence of these moduli was determined by Marshall.[18]

This brief survey shows that a considerable amount of work has been done on the elastic constants of the sodium chloride type halides and that more work is desirable, in particular on cesium chloride type salts. A survey of the availability of cesium chloride type compounds showed that pure single crystals of CsBr and CsI were the most readily available and consequently they were selected as the object of this investigation.[19]

APPARATUS AND PROCEDURE

The CsBr and CsI samples were secured from the Elyria branch of the Harshaw Chemical Corporation. At this plant, optical-quality cesium salt crystals are grown from the melt by a modified Bridgman method. Our CsBr sample was approximately cylindrical, having a length of 0.75 in. and a diameter of 1.5 in. The CsI

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* Now at Delco Radio, Kokomo, Indiana.

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sample was almost a cube with a 1-in. long edge. Both of these crystals were carved from larger ingots. The total impurity content of these salts is less than 10 ppm, the impurities being Al, Ca, Fe, Mg, Cu, Si, and Tl. The rubidium crystals were obtained from the Korth Physical Laboratory and they were approximately cubic with a 1-in. base.

Since CsBr and CsI were not cleaved specimens they had to be oriented by x-ray methods before they were cut. Before taking a Laue back-reflection picture, the specimen was "water polished" in order to obtain well-defined spots. This polishing procedure consisted of rubbing the specimen against a slightly dampened tissue, clamped tight in a ring. Exposures were taken at random until a symmetry pattern was found. From this point on the orientation, work proceeded using the standard method.[20] The oriented specimen was later polished with several grades of Clover lapping compound until its faces were flat and parallel. A parallelism of 30 μin./in. was achieved by handlapping of the crystals on surface ground meonite plates. The parallelism was checked on a Pratt and Whitney Supermicrometer.

At room temperature, salol (phenyl salycilate) served as the acoustical coupling agent, while in the range from 0°C down to -120°C the bonding cement was glycerin. A Dow Corning silicone rubber, Silastic 135, gave a satisfactory coupling film below -120°C.

The cryostat consisted of a heavy copper block, copper flanges, and a stainless steel tube leading into the block. The block and the flanges equalized the chamber temperature to within 0.1°C, while the stainless steel tube minimized the heat losses from the system. The liquid nitrogen was pumped into a Dewar flask in which the above apparatus was suspended. The sample was pressed slightly against a coaxial connecter in such a way that central and peripheral parts of the transducer plating made contact with the middle and ground electrodes of the connector. With this arrangement electrical contact was assured at all temperatures. The temperature was monitored by two pairs of copper-constantan thermocouples and a K-2 potentiometer. The thermocouples were calibrated at the ice point and dry ice point and at the boiling point of liquid nitrogen. The rate of the temperature change was obtained by a Brown Recorder.

The wave velocities were determined by a modified pulsed ultrasonic method. An ultrasonic interferometer was constructed[21] according to the procedure of Williams and Lamb.[22] The method is based on phase interferometry whereby an incoming traveling wave train is cancelled, after it has been reflected from the free end of the sample, by another pulse, which has the same amplitude and frequency as the first, but differs in phase exactly 180°. Consequently, the equipment was designed to generate two pulses with a variable time separation between them. The tops of both of these pulses are flat and the amplitude of the second pulse is adjustable. The first pulse is applied to the crystal, travels down the sample, and is reflected back from the free end of it. When this pulse reaches the transducer, the second pulse is adjusted to be equal to the returning amplitude of the first pulse and the second pulse will cancel the first one, yielding a well-defined null (unrectified echoes are displayed at 10 Mc/sec). From the frequencies at which the nulls occur and the length of the sample, the velocity of the sound wave may be calculated. This method enhances the precision of the velocity measurements, since only a frequency determination is required here instead of a time measurement. A relative precision of 50 ppm is easily achieved with the above system. Another advantage of this method is that it avoids the end effect, since one observes the cancellation in the central portion of the individual pulses, where they are well approximated by a continuous wave.

TABLE I. The measured ρV^2 values for CsBr as a function of temperature in units of 10^{11} d/cm². The figures were obtained from curves drawn through the experimentally determined points. For the limits of error in the last significant figure, see the text.

T (°K)	ρV_1^2 $(C_{11}+C_{12}+2C_{44})/2$	ρV_2^2 (C_{44})	ρV_3^2 $(C_{11}-C_{12})/2$
80	3.1375	0.9622	1.1740
100	3.1018	0.9421	1.1670
120	3.0663	0.9220	1.1600
140	3.0300	0.9019	1.1528
160	2.9937	0.8818	1.1455
180	2.9575	0.8617	1.1381
200	2.9213	0.8416	1.1308
220	2.8850	0.8215	1.1235
240	2.8490	0.8014	1.1160
260	2.8125	0.7813	1.1085
280	2.7775	0.7612	1.1012

RESULTS AND CONCLUSIONS

The three independent velocities in the [110] direction, a compressional mode and two shear modes (polar-

TABLE II. The measured ρV^2 values for CsI as a function of temperature in units of 10^{11} d/cm². The figures were obtained from curves drawn through the experimentally determined points. For the limits of error in the last signfiicant figure, see the text.

T (°K)	ρV_1^2 $(C_{11}+C_{12}+2C_{44})/2$	ρV_2^2 (C_{44})	ρV_3^2 $(C_{11}-C_{12})/2$
80	2.5135	0.8083	0.9543
100	2.4810	0.7919	0.9505
120	2.4490	0.7752	0.9454
140	2.4165	0.7586	0.9401
160	2.3835	0.7421	0.9348
180	2.3515	0.7256	0.9296
200	2.3190	0.7093	0.9242
220	2.2865	0.6928	0.9190
240	2.2550	0.6763	0.9136
260	2.2220	0.6599	0.9083
280	2.1900	0.6434	0.9030

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ized in the [100] and [110] directions) suffice to determine the three elastic constants of the salts examined. In Tables I and II the values for the measured quantities ρV_1^2 $[(C_{11}+C_{12}+C_{44})/2]$, ρV_2^2 (C_{44}) and ρV_3^2 $[(C_{11}-C_{12})/2]$ are shown as a function of temperature. The temperature dependence of the calculated quantities C_{11} and C_{12} and of the measured quantity C_{44} are shown in Fig. 1. Table III compares the room temperature values of the CsBr, CsI, RbBr, and RbI constants with the values of Bolef and Menes,[17] those of Marshall,[18] and the results of Spangenberg and Haussuhl.[16]

The relative precision of a particular ρV^2 determination at a given temperature is limited by the reproducibility of the ultrasonic interferometer. A reading on this instrument is reproducible to within 50 ppm, enabling one to report a particular ρV^2 with a precision of 100 ppm. The absolute accuracy is affected by the uncertainty in density, by the misalignment of the sample axis with respect to the true crystallographic axis, and by the thickness of the adhesive film between the sample and the transducer. Interference due to limited specimen size and diffraction due to finite transducer size also contribute to the total error in the absolute velocity. The fact that phase and group velocity are different in our case would give rise to an additional source of error. The theory incorporates corrections for the change of phase angle with frequency at the transducer. The room temperature density was obtained from x-ray powder values (ASTM) and the temperature dependence of this density was arrived at by extrapolating the density data in the Critical Tables. The inaccuracy in the constants due to misalignment was estimated according to Waterman.[23] A bond thickness correction was made, accounting for the sound velocity in the adhesive. The estimated total error in absolute accuracy for a particular velocity measurement is approximately 0.05%. The estimated errors in C_{11}, C_{12}, and C_{44} of the particular specimen used are ±0.2%, ±0.5% and ±0.1%, respectively.

TABLE III. Comparison of room temperature values of RbBr, RbI, CsBr, and CsI constants in units of 10^{11} d/cm² with the values of Bolef and Menes and with the results of Spangenberg and Haussuhl.

		Present investigation	Bolef and Menes	Spangenberg and Haussuhl
RbBr	C_{11}	3.15	3.17	3.185
	C_{12}	0.493	0.42	0.48
	C_{44}	0.384	0.388	0.385
RbI	C_{11}	2.54	2.56	2.585
	C_{12}	0.407	0.31	0.375
	C_{44}	0.276	0.287	0.281
CsBr	C_{11}	3.097	3.00	3.056
	C_{12}	0.903	0.78	0.776
	C_{44}	0.7500	0.756	0.743
CsI	C_{11}	2.434	2.46	
	C_{12}	0.636	0.67	
	C_{44}	0.6316	0.624	

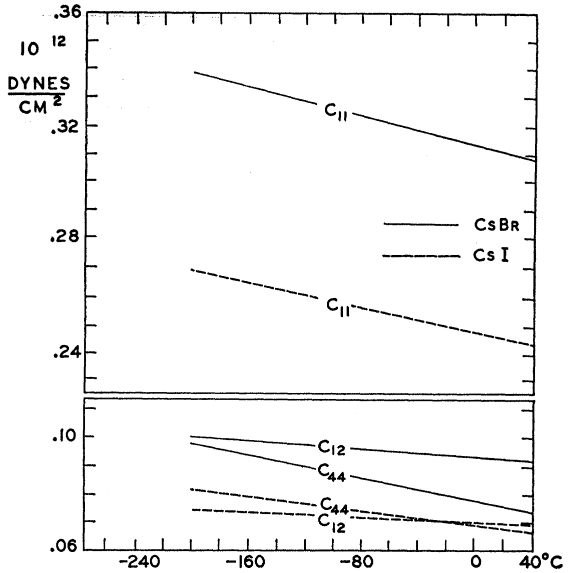

FIG. 1. The temperature dependence of the adiabatic elastic constants of CsBr and CsI.

DISCUSSION OF THE ELASTIC BEHAVIOR OF ALKALI HALIDES

In Figs. 2–4 the available data on C_{11}, C_{12}, and C_{44} for all alkali halides were plotted against the respective radii of the alkali ions. Observing Fig. 2, one sees that there is no marked difference in behavior of C_{11} as one goes from the sodium chloride type lattice to a cesium chloride type one. A physically reasonable explanation of this result is apparent, if one examines the nearest-neighbor interaction for uniaxial compression. In a sodium chloride type lattice, nearest neighbors are pressed

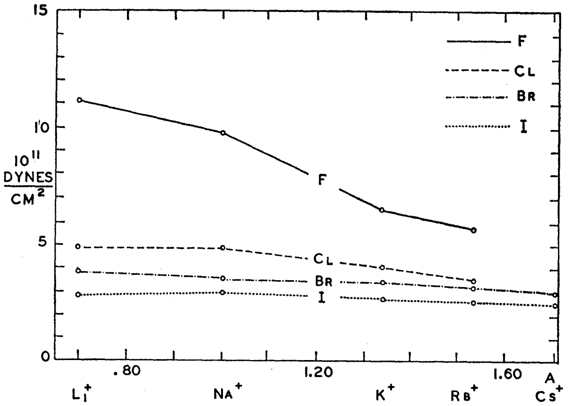

FIG. 2. The room temperature C_{11} as a function of the alkali ion radii.

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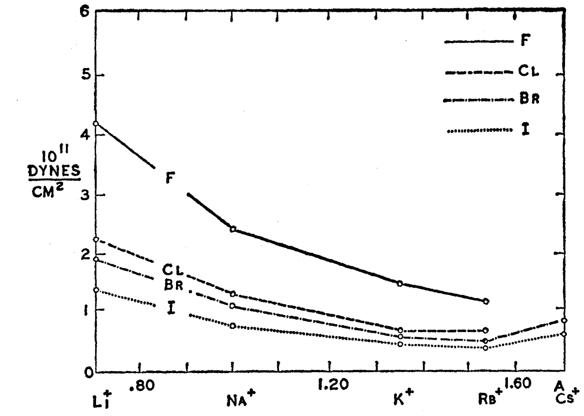

FIG. 3. The room temperature C_{12} as a function of the alkali ion radii.

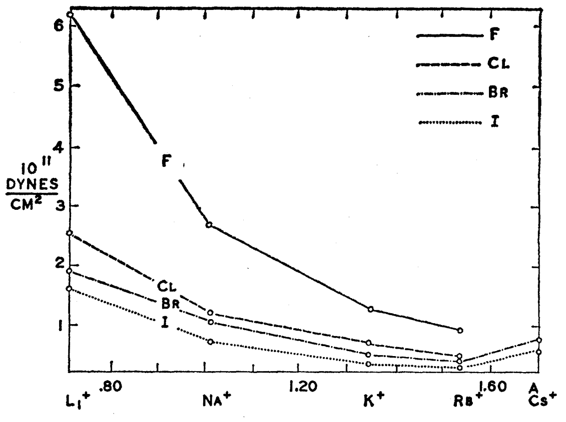

FIG. 4. The room temperature C_{44} as a function of the alkali ion radii.

directly against each other, while in a cesium chloride type lattice the compressive force is divided among the nearest neighbors, four ions in the cube corner positions pressing against the body-centered ion. The data presented indicate that these two unlike interactions produce a comparable change in length for a particular applied stress. The results are implicit in the theories of Fuchs[24] and Krishnan and Roy.[25] On the other hand, from an inspection of Figs. 3 and 4, drawn for C_{12} and C_{44}, it is obvious that the values for C_{12} and C_{44} for the cesium salts are higher than would be expected, if they had a sodium chloride type structure. Considering the C_{44}-type shear motion of lattice planes [a (100) lattice plane slipping with respect to the other] one finds that it is easier to slide a plane in a sodium chloride type lattice than in a cesium chloride type one, since in the first case one is moving the ions away from a closed-shell repulsion potential maximum, while in the latter case the closed shell repulsion potential is a minimum at the equilibrium configuration. It follows that C_{12} and C_{44} for the body-centered halides are larger, meaning that CsBr and CsI are stiffer in shear than would be expected if their structure had been the face-centered variation. This result also has been surmised by Fuchs and by Krishnan and Roy.

On Figs. 5 and 6 the measures of the anisotropy $[(C_{11}-C_{12})/2C_{44}]$ and of the ratio $2(C_{12}-C_{44})/(C_{12}+C_{44})$ are plotted for most of the alkali halides. From Fig. 5 one observes that the anisotropy of lithium salts stays constant regardless of the halide ion combined with the lithium. One also observes that as the atomic number of the halide ion increases, the nature of the alkali ion manifests itself more by making the heavier salts for the same halide ion more anisotropic. For the body-centered salts the general linear characteristic of the curve is broken and the anisotropy of the cesium salts is close to one, a value substantially lower than that of the immediately preceding sodium chloride type rubidium salts.

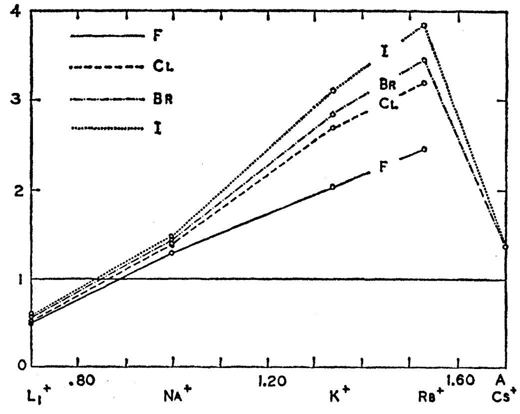

FIG. 5. The measure of the room temperature anisotropy $(C_{11}-C_{12})/2C_{44}$ as a function of the ion radii.

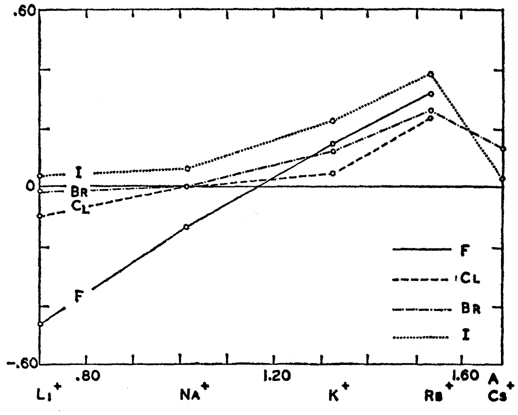

FIG. 6. The measure of the room temperature ratio $(C_{12}-C_{44})/\frac{1}{2}(C_{12}+C_{44})$ as a function of the alkali ion radii.

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TABLE IV. Elastic constants of alkali halides at low temperatures in units of 10^{11} d/cm^2.[a]

	F	Cl	Br	I
		C_{11}		
Li	12.42_H			
Na		5.730_N		
K		4.832_H	4.17_H	3.38_H
Rb				
Cs			3.355_N	2.669_N
		C_{12}		
Li	4.24			
Na		0.986		
K		0.54	0.58	0.22
Rb				
Cs			1.002	0.753
		C_{44}		
Li	6.49			
Na		1.32		
K		0.663	0.505	0.368
Rb				
Cs			0.972	0.814

[a] Subscript H—at liquid helium temperature; subscript N—at liquid nitrogen temperature.

As a possible explanation for the same anisotropy value for all lithium halides, one surmises that the halide ions touch each other in lithium salts and that the lithium ions occupy the available holes in the lattice. For salts where the alkali ion size is larger, the value of the anisotropy increases, since the lattice departs from being a simple face-centered cubic lattice. For the other alkali ions, increasing the halide ion size also increases the anisotropy of the salt. When considering cesium chloride type halides, the observed sudden drop in the value of the anisotropy may be due to the increased number of nearest neighbors tending to make the crystal more isotropic.

The meager low-temperature data in Table IV indicates that as the temperature is lowered, the anisotropy increases in general, while the departure from the Cauchy relation is decreased as a rule. The scarce temperature-dependent data on C_{12} and C_{44} would also suggest that the slopes for the above two constants are somewhat coupled (possibly by the Cauchy relation), the slope of C_{12} being, as a rule, less than that of C_{44} for any particular salt.

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Spin-Wave Contribution to Specific Heat and Magnetization in Canted Spin Arrays

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The dispersion law for spin waves in a cubic canted spin array has been derived. From this dispersion law the spin-wave contributions to the specific heat and magnetization have been obtained. The integrals involved in the expressions for these quantities have been evaluated numerically for a moderate range of the system description parameters B and F. In a special case the behavior of the spin wave contribution has been shown to change from $T^{\frac{3}{2}}$ at very low temperature to T^3 at somewhat higher temperatures. This phenomenon is discussed in terms of some available data on low-temperature spin system specific heats.

INTRODUCTION

THE subject of spin waves has been of interest ever since Bloch[1] initially proposed the method as a way of describing the deviations of the magnetization at low temperatures from that at absolute zero. Recent direct observations of the spin-wave resonance[2] have tended to increase our faith in the model. An excellent review[3] includes calculations typical of those to be found in the literature.

One of the most interesting facets of spin-wave theory is the study of such waves in canted arrays. This interest was stimulated by Dzyaloshinsky's[4] observation that the observed weak transverse ferromagnetism[5] of α-Fe_2O_3 could be explained in terms of a turning towards one another of the two antiferromagnetically coupled sublattices. This in turn could reasonably be due to canted anisotropy fields. Orbach[6] has pursued this question from the spin-wave viewpoint and has obtained the spin-wave dispersion law and the static magnetization due to canted arrays.

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