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INFLUENCE OF PRESSURE UP TO 20 kbar ON THE ELASTIC PROPERTIES OF RUBIDIUM CHLORIDE AND IODIDE

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An ultrasonic pulse method was used to measure the velocities of propagation of longitudinal and transverse waves in rubidium chloride and iodide at pressures from 0 to 20 kbar. The occurrence of a polymorphic transition from the NaCl-type structure to the CsCl-type structure was confirmed for RbCl at pressures of 5.5 kbar and for RbI at 3.9 kbar. The elastic moduli K_S, K_T, E, G, σ and the Debye temperature Θ were calculated for both phases of each compound up to 20 kbar. It is shown that the values of the pressure at which the polymorphic transition took place and the pressure dependences of the isothermal bulk moduli K_T of RbCl and RbI, calculated using Born's model, are in satisfactory agreement with the experimental data.

ALKALI-halide crystals have been investigated very intensively because they can be represented quite well by the simple ionic lattice model. There has been and still is special interest in the problems of the stability of the observed crystalline structures and the possibility of polymorphic transitions under the influence of pressure and temperature. From Slater's[1] and Bridgman's[2] investigation, it is known that the halides RbCl, RbBr, and RbI, which have the NaCl-type structure at room temperature and atmospheric pressure, undergo a polymorphic transition to the CsCl-type structure[3, 4] at pressures of 5.4, 4.5, and 3.9 kbar, respectively. This transition is accompanied by a considerable sudden change in volume: 14% for RbCl, 13% for RbBr, and 12.5% for RbI.[2] An examination of the p–V dependences of rubidium halides shows that the change in the internal energy, which accompanies the polymorphic transition in these salts, represents a very small fraction of the lattice energy of either phase of these compounds. The difference between the energies of the two lattices at the transition pressures of rubidium halides can be equated to the mechanical work needed to produce this transition because the transition pressure is almost independent of temperature. The experimental values of the mechanical work done to produce the transition in rubidium halides are 0.7–0.9 kcal/mole, which represent 0.5–0.7% of the lattice energy. Consequently, both the problem of the theoretical prediction of the stability of different structures of these compounds and the calculation of their polymorphic transition pressures require high accuracy in the calculation of the energies of the different phases of any one compound.

Much interest has been displayed in the calculation of the transition pressures for various alkali-halide compounds, including rubidium halides. Thus, Born and Mayer[5] have shown that, at atmospheric pressure and room temperature, the stable phase of all halides should be the NaCl-type structure, but experiment shows that under these conditions CsCl, CsBr, and CsI crystallize in the CsCl-type structure. The estimates of the transition pressures for various alkali halides, obtained by Jacobs[4] using the Born-Mayer model, are considerably higher than the experimentally determined pressures. It should be mentioned that it is usual to employ Bridgman's data on the p–V dependence in the calculation of the energies of various phases of alkali-halide crystals using Born's model and in the estimates of the parameters of these models.

The large discrepancy between the experimentally observed transition pressures of various alkali-halide salts and the values calculated using Born's model may be due to the imperfection of the model itself and the inaccuracy of the experimental data on the p-V dependence, used to determine the parameters which occur in Born's expression for the energy. To determine Born's repulsion parameter ζ, it is necessary to know the compressibility as a function of pressure—and ζ is very sensitive to errors in the determination of the compressibility. The piezometric measurements of Bridgman do not yield the compressibility directly as a function of pressure. The compressibility is found by differentiating the experimental dependence $\Delta V/V_0 = f(p)$ with respect to pressure, a process which is known to give rise to considerable errors.

The purpose of the present investigation was to refine the data of the compressibility of RbCl and RbI under pressure, because the ultrasonic method of measuring the elastic moduli of solids under pressure allows us to determine the compressibility as a function of pressure directly from the measured velocities of propagation of longitudinal and transverse waves in a crystal. It was interesting to check the applicability of Born's model to RbCl and RbI, using these refined data to calculate the polymorphic transition pressure and the isothermal bulk modulus as a function of pressure for the high-pressure and low-pressure phases.

1. EXPERIMENT

In our investigation of the elastic properties under pressure by an ultrasonic pulse method,[6] we used RbCl and RbI samples of "pure" grade. A finely ground powder of a salt was dried in a dessicator at 150° C for 1.5–2 days and was then compacted into cylindrical pellets in a vacuum press by applying a pressure of 15–17 kbar for an hour. The density of semitransparent pellets (20 mm in diameter and 6–10 mm thick) was 2.81 g/cm^3 for RbCl and 3.55 g/cm^3 for RbI.

At 298° K and atmospheric pressure, we determined the velocities of propagation of longitudinal

Table I. Elastic properties of RbCl under pressure.

	p, kbar							% change at transition	% change at Pmax	Relative error (%) in slope
	0	3	5,5	8	12	16	20			
$10^{-5}\,v_l$, cm/sec	3.101	3.168	3.224					6.0	19.9	±0.2
			3.409	3.478	3.572	3.654	3.718			
$10^{-5}\,v_t$, cm/sec	1.688	1.690	1.691					13.4	20.1	±0.3
			1.918	1.939	1.972	2.002	2.027			
ρ, g/cm^3	2,818	2.868	2.910					19.2	29,6	±0,05
			3.450	3.488	3.547	3.601	3.651			
$10^{-11}\,K_S$, dyn/cm^2	1.64	1.78	1.92					24.7	86,7	±0.93
			2.32	2.47	2.69	2.88	3,07			
$10^{-11}\,E$, dyn/cm^2	2.07	2.13	2,18					50.4	87.3	±0.43
			3.22	3.35	3.53	3.71	3.88			
$10^{-11}\,K_T$, dyn/cm^2	1.58	1.71	1.83					24.4	84.2	±0.90
			2.22	2.35	2.56	2.74	2.90			
$10^{-11}\,G$, dyn/cm^2	0.803	0.819	0.832					54,6	87.1	±0.65
			1.270	1.310	1.380	1.440	1.500			
σ	0.289	0.301	0.310					—14.4	— 0.3	±1.0
			0.268	0.274	0.281	0.286	0.288			
Θ, °K	135.2	136.4	137.3					19.7	31.1	±0.4
			164.0	166.6	170.4	174.0	177.4			

Note. Upper rows of values represent the low-pressure phase, and lower rows the high-pressure phase.

Table II. Elastic properties of RbI under pressure.

	p, kbar							% change at transition	% change at Pmax	Relative error (%) in slope
	0	2	3,9	6	8	10	12			
10^{-5} v_l, cm/sec	2.219	2.262	2.307					5.8	20.2	±0.20
			2.436	2.501	2.561	2.615	2.667			
10^{-5} v_t, cm/sec	1.156	1.152	1.150					14.2	21.1	±0.36
			1.314	1.342	1.364	1.384	1.400			
ρ, g/cm³	3.565	3.631	3.689					15.5	24.8	±0.03
			4.240	4.300	4.353	4.404	4,450			
10^{-11} K_S, dyn/cm²	1.12	1.22	1.31					19.3	79.4	±0.98
			1.54	1.66	1.77	1,89	2,01			
10^{-11} E, dyn/cm²	1.252	1.278	1.302					47.4	83.2	±0.52
			1.896	2.007	2.109	2.205	2.293			
10^{-11} K_T, dyn/cm²	1.06	1.15	1.24					19.8	75.5	±0.90
			1.45	1.55	1.66	1.76	1,87			
10^{-11} G, dyn/cm²	0.476	0.482	0.488					51.3	83.6	±0.77
			0.732	0.774	0.810	0.844	0.875			
σ	0.314	0.325	0.335					—12.8	— 1.2	±0.98
			0.294	0.298	0.302	0,306	0.310			
Θ, °K	83.3	83.6	84.0					19.2	+30.6	±0.35
			100.0	102.6	104.9	107.0	108.8			

Note. Upper rows of values represent the low-pressure phase, and lower rows the high-pressure phase.

and transverse waves in RbCl and RbI samples of various thicknesses (Tables I and II).

In the calculations of the elastic moduli at room temperature (298° K) and atmospheric pressure (p_0), we used the density values determined from the lattice parameters. For RbCl we used $\rho_0 = 2.818$ g/cm³ and for RbI, $\rho_0 = 3.565$ g/cm³, which were in good agreement with the experimentally determined values of the density at 298° K and atmospheric pressure. The relative errors in the determination of the initial values of the moduli (at atmospheric pressure and 298° K) were 1.5% for K_S, 0.2% for E and G, and 0.8% for σ.

We used an ultrasonic pulse method in a high-pressure apparatus[7] to measure simultaneously the change in the transit times of longitudinal (Δt_l) and transverse (Δt_t) waves of 3–5 Mc frequencies at pressures up to 20 kbar for RbCl and up to 12 kbar for RbI. At the same time we measured the change in the sample thickness Δl with pressure. The force F, applied to a high-pressure plunger, was measured with a strain dynamometer and recorded automatically with a potentiometer of the ÉPP-09 type, which made it possible to eliminate the friction in the press from our calculations. The pressure in the high-pressure chamber was calculated from the ratio F/S (S was the area of the high-pressure plunger) with an accuracy up to 100 bar.

The experimentally determined dependences $\Delta t_l(p)$, $\Delta t_t(p)$ and $\Delta l(p)$ confirmed the occurrence of a polymorphic transition in both salts, manifested by a continuous change in the values of Δt and Δl at a fixed pressure: in the case of RbCl, this happened at 8–10 kbar when the pressure was increasing and at 3–1.5 kbar when it was decreasing; for RbI, the same happened in the pressure ranges 4.7–5.9 and 3–2.2 kbar, respectively. The transition pressure was defined as the average pressure between the beginning of the transition with the pressure increasing and decreasing; it amounted to 5.5 kbar for RbCl and 3.9 kbar for RbI, in good agreement with Bridgman's data.[2]

When the friction in the high-pressure chamber was subtracted the polymorphic transition in these salts was found to have a hysteresis loop. The width of this loop was 4.7 kbar for RbCl and 1.6 kbar for RbI. The volume discontinuity at the transition was 15.24% for RbCl and 12.55% for RbI.

To calculate the elastic moduli and the Debye temperatures of these salts under pressure, we determined the velocities of propagation of longitudinal and transverse waves and the density of these compounds using the following expressions:[7]

$$v(p) = v_0 + \frac{l_0 - \Delta l(p)}{l_0/v_0 - \Delta t(p)}, \tag{1}$$

$$\rho = \rho_0 + \left[1 + \frac{\alpha^2 T}{c_p}\left(v_{l0}^2 - \frac{4}{3}v_{t0}^2\right)\right] \int\limits_0^p \frac{dp}{v_l^2(p) - {}^4/_3 v_t^2(p)}, \tag{2}$$

where l_0 and v_0 are, respectively, the thickness of the sample and the velocity of propagation of the corresponding waves at atmospheric pressure and 298° K; α is the volume thermal expansion coefficient which is 9.85×10^{-5} deg^{-1} for RbCl and

11.9×10^{-5} deg^{-1} for RbI; c_p is the specific heat at constant pressure, which is 12.3 cal-deg^{-1} mole^{-1} for RbCl and 12.5 cal-deg^{-1} mole^{-1} for RbI. Integration of Eq. (2) is possible up to a discontinuity of the first kind in the function $[v_l^2(p) - {}^4/_3 v_t^2(p)]^{-1}$, found at the phase transition.

Thus, the dependence $\rho(p)$ was calculated for the low-pressure phases of rubidium chloride and iodide at 0–5.5 and 0–3.9 kbar, respectively. The density of the high-pressure phase at the transition pressure was determined from our data on the volume discontinuity at the transition using the formula:

$$\rho_t{}^* = \left[\frac{1}{\rho} - \frac{1}{\rho_0}\frac{\Delta V}{V_0}\right]^{-1}, \tag{3}$$

where ρ_0 and ρ_t are, respectively, the densities of the low-pressure phase at atmospheric pressure and at the transition pressure. For the high-pressure phase, the dependence $\rho(p)$ was determined from Eq. (2) for RbCl, and RbI at 5.5–20 and 3.9–12 kbar respectively, replacing ρ_0 in Eq. (2) with ρ_t^* and substituting for v_{l0} and v_{t0} the values of the velocities of propagation of longitudinal and transverse waves in the high-pressure phase at the transition pressure p_t.

Figure 1 shows the dependences $v_l(p)$, $v_t(p)$, and $\rho(p)$ for both phases of each compound. The same figure includes, for comparison, Bridgman's data on the density ρ,[8] denoted by crosses.

Tables I and II list, for RbCl and RbI, the values of the bulk modulus (adiabatic K_S and isothermal K_T), Young's modulus E, the shear modulus G, Poisson's ratio σ, and the Debye temperature Θ calculated from the experimental data on both velocities and on the density at various pressures. The same tables include the values of the relative changes in these quantities at the transition pressure and at the maximum pressure (p_{max}) as well as the relative error in the determination of these quantities under pressure. A characteristic feature of the pressure dependence of these quantities is their weak rise with pressure for the first phase, a sudden increase at the transition (with the exception of Poisson's ratio σ, which decreases suddenly at the polymorphic transition), and a much more rapid change with pressure in the second phase. It should be mentioned that the slopes of the pressure dependences of the moduli K_S and K_T are approximately the same for both phases, as mentioned by Slater.[1]

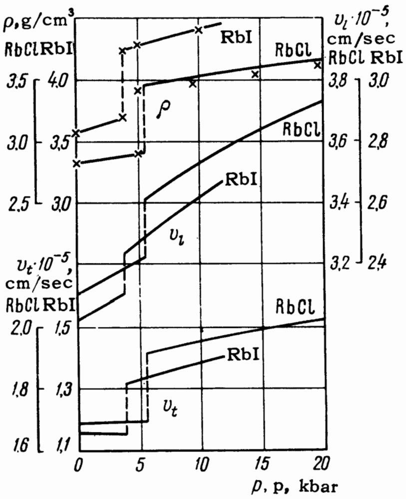

FIG. 1. Pressure dependences of the velocities of longitudinal (v_l) and transverse (v_t) waves and of the density (ρ) of RbCl and RbI. Crosses represent Bridgman's data. [8]

Table III lists the coefficients which occur in the expansion of the isothermal compressibility

$$\varkappa_T = 1 / K_T = a - 2bp + 3cp^2$$

for both phases of RbCl and RbI, and the coefficients in the expansion of the dependence

$$-\Delta V / V_0 = ap - bp^2$$

found on Bridgman's[9] and Slater's[1] data.

The weak rise of G and the practically constant v_t under pressure, observed for the NaCl-type structure of these salts, can be explained by writing the effective shear modulus of a polycrystalline sample

$$G = \rho v_t^2 = {}^3/_5 c_{44} + {}^2/_5 [(c_{11} - c_{12}) / 2]$$

in terms of the elastic moduli of a single crystal,[10] where c_{44} and $(c_{11} - c_{12})/2$ are the moduli of a single cubic crystal representing the resistance to shear along different directions. From experiments on a potassium chloride single crystal, which undergoes a polymorphic transition under pressure, changing from the NaCl-type structure to the CsCl-type structure, it is known that $(c_{11} - c_{12})/2$ increases and c_{44} decreases with pressure, while in NaCl, whose analogous transition is

Table III

Substance *		$10^{12}\, a$, cm^2/dyn	$10^{24}\, b$, cm^4/dyn^2	$10^{35}\, c$, cm^6/dyn^3
RbCl	l.p.	6.34; 6.65[9]	87.5; 163.1[9]	
	h.p.	5.16	66.5	81.24
RbI	l.p.	9.40; 9.56[1]	182.2; 205,6[1]	
	h.p.	7.91	139.3	184.5

* Here "l.p." is the low-pressure phase, and "h.p." the high-pressure phase.

retarded at room temperature, c_{44} increases weakly with pressure.[11] Burger[12] suggests that the decrease in c_{44} with pressure is associated with the mechanism of the polymorphic transition in rubidium and potassium halides. Since the contribution of c_{44} to the effective shear modulus represents 60%, it is probable that its decrease influences the weak pressure dependence of G and v_t.

2. SOME CALCULATIONS USING BORN'S MODEL

All previous calculations of the transition pressure in alkali halides have been based on Löwdin's hypothesis[13] that the Born's repulsion parameter ζ is independent of the crystal structure of the substance undergoing a polymorphic transition. To check this hypothesis, we calculated the Born repulsion parameters for RbCl and RbI.

To determine the Born repulsion parameters from the data on the elastic properties of polycrystalline samples and to find the behavior of these parameters under pressure and after transition to a new phase, we used the vibrational form of Hildebrand's equation of state and its derivative with respect to volume at constant pressure:

$$\frac{dW_L}{dV} = -\left(p - T\frac{\alpha}{\varkappa_T}\right), \tag{4}$$

$$V\frac{d^2W_L}{dV^2} = \frac{1}{\varkappa_T}\left\{1 + \frac{T}{\varkappa_T}\left[\left(\frac{\partial\varkappa_T}{\partial T}\right)_p + \frac{\alpha}{\varkappa_T}\left(\frac{\partial\varkappa_T}{\partial p}\right)_T\right]\right\}. \tag{5}$$

(Here, W_L is the energy of a static crystal.) The use of this form of the equation of state is fully justified because the Debye temperatures of our salts at the transition pressure are considerably lower than room temperature and, for the CsCl-type structure, they do not exceed by more than 20% the corresponding characteristic temperatures of the NaCl-type phase at atmospheric pressure.

According to Born's model, the energy of a static crystal, regarded as a function of the distance between nearest neighbors of opposite charge, can be written as follows:

$$W_L(r) = N_A\left(-\frac{\alpha_M e^2}{r} - \frac{C}{r^6} - \frac{D}{r^8} + MBe^{-r/\zeta}\right), \tag{6}$$

where α_M is Madelung's constant; e is the electronic charge; N_A is Avogadro's number; M is the coordination number; C and D are van der Waals' constants, taken from Mayer's paper;[14] r is the shortest distance between oppositely charged ions.

Using the equation of state (4) for a crystal and substituting Eq. (6) in Eq. (5), we obtain expressions for the calculation of the parameters B and ζ:

$$B = \zeta\left[\frac{1}{r_0^2}\left(a_M e^2 + \frac{6C}{r_0^5} + \frac{8D}{r_0^7}\right) - 3T\left(\frac{\alpha}{\varkappa_T}\right)_0 s r_0^2 e^{r_0/\zeta}\right]; \tag{7}$$

$$\begin{aligned}\frac{1}{\varkappa_T}\left\{1 + \frac{T}{\varkappa_T}\left[\left(\frac{\partial\varkappa_T}{\partial T}\right)_p + \frac{\alpha}{\varkappa_T}\left(\frac{\partial\varkappa_T}{\partial p}\right)_T\right]\right\} \\ = -\frac{1}{9sr^4}\left(4\alpha_M e^2 + \frac{54C}{r^5} + \frac{88D}{r^7}\right) \\ + \frac{1}{9sr\zeta}\left(\frac{1}{\zeta} + \frac{1}{r}\right)Be^{-r/\zeta};\end{aligned} \tag{8}$$

here s is the structure parameter, which is 2 for the NaCl type structure and 1.54 for the CsCl-type structure; r_0, κ_{T0} and r, κ_T are, respectively, the interionic distance and compressibility at atmospheric pressure p_0 and at the transition pressure p_t. The experimental data used are collected in Table IV. The values of $(\partial\kappa_T/\partial T)_p$ were taken from Slater's[1] and Bridgman's[9] investigations. The values of r_0 and κ_{T0} for the high-pressure phases of both salts were found by extrapolation of the r(p) and κ_T(p) curves to zero pressure for these phases.

The repulsion parameter was calculated at atmospheric and transition pressures for both phases of each compound. It was then found that the repulsion parameter for a given substance remained constant, within the limits of the accuracy of the calculation (±0.005 Å), not only when the pressure applied to a given phase was increased, but also on transition to a second phase, which confirmed Löwdin's hypothesis[13] that the values of ζ were equal for different phases of alkali-halide salts. For RbCl, the repulsion parameter was found to be 0.295 ± 0.004 Å and for RbI, 0.331 ± 0.002 Å.

To determine whether Born's model can be used in the calculation of the transition pressures of these two rubidium halides, it was desirable to calculate the difference between the energies of the two phases at the polymorphic transition. For RbCl, this difference was 1.54 kcal/mole; for RbI, it was 2.7 kcal/mole. The values of pΔV for RbCl and RbI calculated from experiments were 0.8 and 0.7 kcal/mole, respectively. Such a large discrepancy between the experimental data and those obtained from the calculations based on Born's model was due to the uncertainty in the estimates of the energies of the two phases because of the departure of these halides from Cauchy's relationship. Seitz showed[15] that, for a 30% deviation from Cauchy's relationship, which was the case for

Table III. Coefficients in the expansion for the isothermal compressibility of the RbCl and RbI.

Substance	P_t, kbar	Phase	$10^8 r$, cm		$10^{12}\kappa_T$, cm^2/dyn		$10^{-7}\alpha/\kappa_T$, dyn.cm^{-2}.deg^{-1}		$10^4\Lambda$, deg^{-1}	
			p_0	p_t	p_0	p_t	p_0	p_t	p_0	p_t
RbCl	5.5	l.p.	3.290	3.255	6.34	5.46	1.55	1.80	4.0	4.6
		h.p.	3.384	3.355	5.16	4.51	1.91	2.20	5.2	6.4
RbI	3.9	l.p.	3.670	3.628	9.41	8.10	1.26	1.47	2.2	2.8
		h.p.	3.816	3.780	7.91	6.90	1.50	1.72	3.2	3.9

Note. Here we use the notation: $\Lambda = \kappa_T^{-1}[(\partial\kappa_T/\partial T)_p + (\alpha/\kappa_T)(\partial\kappa_T/\partial p)_T]$

RbCl and RbI, the uncertainty in the estimate of the energy using Born's model was 3%, i.e., 5 and 4.5 kcal/mole for RbCl and RbI, respectively. Hence, it follows that there is no point in including van der Waal's terms in the expression for the energy (6) because their contribution to the absolute value of the energy is only 2 kcal/mole.

Since the accuracy of the measurement of the compressibility and density as a function of pressure influences greatly the results of the calculations of the energy, the polymorphic transition pressure, and other energy properties of a crystal treated using Born's model, it was of interest to estimate the transition pressure and the isothermal bulk modulus for both phases of RbCl and RbI using Born's simplified model (without allowance for van der Waals' terms), using the data of our measurements to estimate the repulsion parameters ζ and B in the expression for the energy.

For this calculation, following Löwdin's earlier investigation,[13] we can use the following expression for the energy of a static crystal:

$$W_L(r) = N_A\left[-\frac{\alpha_M e^2}{r} + MBe^{-r/\zeta}\right]. \tag{6a}$$

The parameter B is determined from the condition of equilibrium of a static crystal at zero pressure. Then, we write the expression for the pressure p and the thermodynamic potential Φ as a function of the interionic distance:

$$p = -\frac{\alpha_M e^2}{3sr^2}\left[\frac{1}{r^2} - \frac{1}{r_0^2}\exp\left(\frac{r_0 - r}{\zeta}\right)\right], \tag{9}$$

$$\Phi = -\frac{4}{3}\frac{\alpha_M e^2}{r} + \frac{\alpha_M e^2}{r_0^2}\left(\zeta + \frac{r}{3}\right)\exp\left(\frac{r_0 - r}{\zeta}\right) \tag{10}$$

Equations (9) and (10) are applied separately to two crystal structures and they include, as unknown parameters, the interionic distance r_0 at atmospheric pressure in the CsCl-type structure and the parameters ζ for both structures. A suitable selection of the values of these parameters allows us to determine the transition pressure by finding the point of intersection of the pressure dependences of the thermodynamic potential for both structures.

On the basis of the calculation of the parameter ζ for RbCl and RbI from Hildebrand's equation of state (described earlier in the present article), we shall assume ζ to be the same for both phases and we shall determine it from the compressibility κ_{T0} and the interionic distance r_0 for the low-pressure phase using the expression

$$\frac{1}{\zeta} = \frac{9sr_0^3}{\alpha_M e^2 \varkappa_{T0}} - \frac{2}{r_0}. \tag{11}$$

For the high-pressure phase, we shall take the value of r_0 to be equal to the sum of the interionic distance at atmospheric pressure in the NaCl-type phase and a correction for the coordination, which is 0.08 Å for the CsCl-type structure.[16] This selection of r_0 for the high-pressure phase results in values of r_0 being 0.01 and 0.07 Å lower than the experimental values for RbCl and RbI.

It should be mentioned that our data on RbCl and RbI and Bridgman's data on potassium and rubidium halides[8] indicate that the correction for the coordination, used in the calculation of the interionic distance in the CsCl-type phase at atmospheric pressure, is not constant but increases with increase of the halogen dimensions.

Calculations of the repulsion parameter ζ using Eq. (11) show that its values are 0.321×10^{-8} and 0.317×10^{-8} cm for RbCl and 0.346×10^{-8} and 0.342×10^{-8} cm for RbI (the two values in each case representing the low-pressure and high-pressure phases, respectively), provided r_0 for the CsCl-type structure is assumed to have the values found by extrapolating the dependence r(p) for the high-pressure phase to zero pressure.

The transition pressures, calculated from the relationships (9) and (10), are 12 kbar for RbCl and 6 kbar for RbI, in good agreement with our experimental data on the transition pressures of these salts. Jacobs[4] used Born's model and Bridgman's data on the p-V dependence to estimate the parameters in Born's expression for the energy, and calculated the polymorphic transition pressures for RbCl and RbI. His values were 39 and 22 kbar, respectively.

It should also be mentioned that, in a recent paper of Lombardi and Jansen,[17] the transition pressure was calculated for a number of alkali halide salts allowing for the three-point interaction: they obtained 7.7 kbar for RbCl and 4.8 kbar for RbI. Thus, we may conclude that the simple central-force model for RbCl and RbI reproduces well the experimental values of the transition pressures.

As expected, the calculation of the pressure dependence of the interionic distance using Eq. (9) gives very good agreement with experiment. Löwdin[13] has already pointed this out. It was interesting to check the discrepancy between the calculated and experimental values for the isothermal bulk modulus, which is the second derivative of the energy of a crystal with respect to volume at constant temperature.

The isothermal bulk modulus was calculated from the expression

$$K_T = \frac{\alpha_M e^2}{9sr^2}\left[\frac{1}{r_0^2}\left(\frac{r}{\zeta}+2\right)\exp\left(\frac{r_0-r}{\zeta}\right)-\frac{4}{r^2}\right]. \qquad (12)$$

Figure 2 gives the pressure dependences of the isothermal bulk modulus calculated by applying Born's model to both phases of each substance. The crosses in Fig. 2 denote the experimental values of K_T. It is evident from Fig. 2 that the calculated and experimental values are in sufficiently good agreement.

CONCLUSIONS

1. An ultrasonic pulse method was used in the pressure range from 0 to 20 kbar to measure the velocities of propagation of longitudinal v_l and transverse v_t waves and calculations were made of the elastic moduli K_S, K_T, E, G, σ and of the Debye temperature Θ of RbCl and RbI, which underwent a polymorphic transition from the NaCl-type structure to the CsCl-type structure at pressures of 5.5 and 3.9 kbar, respectively.

2. A weak increase in the shear modulus G with pressure observed for the NaCl-type phases of both compounds, could be associated with the proposed polymorphic transition mechanism.

3. The data obtained on the pressure dependences of the compressibility and the density allowed us to calculate the repulsion parameters ζ for both phases of RbCl and RbI using Born's expression for the energy and Hildebrand's equation of state. It was found that the repulsion parameter ζ of each compound was not affected by pressure or by transition to a new phase, in agreement with Löwdin's hypothesis.[13]

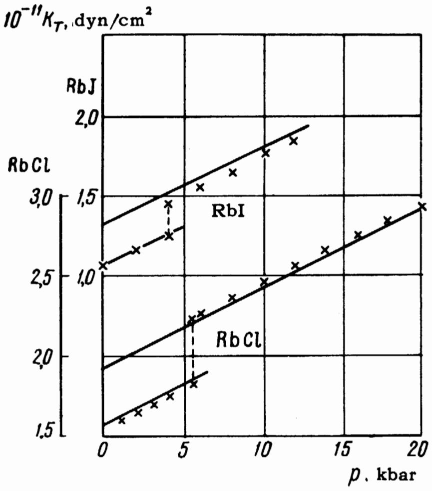

FIG. 2. Pressure dependence of the isothermal bulk modulus of RbCl and RbI: continuous lines represent the results of calculations using Born's model: X – are experimental values.

4. Using Born's expression for the energy and the equation of state for a static crystal, we calculated the transition pressure and the pressure dependence of the isothermal bulk modulus K_T for both phases of RbCl and RbI.

5. The calculated values of the polymorphic transition pressure for RbCl and RbI were in sufficiently good agreement with experiment.

6. A comparison of the calculated values of the transition pressures of RbCl and RbI with the analogous results of Jacobs[4] showed that the results of such calculations were greatly affected by the accuracy of the determination of the pressure dependence of the compressibility.

7. A comparison of our calculated values of the polymorphic transition pressures of RbCl and RbI with the results of the quantum-mechanical calculation of Lombardi and Jansen[17] showed that the simple central-force model was fully satisfactory for such calculations.

8. The pressure dependence of the isothermal bulk modulus K_T, calculated using Born's model reproduced sufficiently well, within the limits of the error, the experimental dependence $K_T(p)$.

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