

Pressure and Temperature Dependence of the Elastic Constants of RbCl, RbBr, and RbI*

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This paper presents the ultrasonic measurements of the elastic constants of RbCl, RbBr, and RbI as a function of pressure up to approximately 4 kbars in the temperature range of 120° to 300°K. The reduction of the raw data is analyzed according to the self-consistent method suggested by Cook and is discussed at length so as to clarify the limitations as well as the precision of the final results presented in this paper. The results of adiabatic as well as the isothermal values of the elastic-constant measurements at pressure are given together. Pressure derivatives of the elastic constants of the above salts under different thermodynamic conditions are calculated and are given separately. Finally the Cauchy relation and anisotropy are discussed.

INTRODUCTION

The elastic constants of solids, correlated with other physical properties, provide a valuable insight into the nature of atomic binding forces. The second-order elastic constants and their pressure dependence provide convenient tests of the theories of cohesion and provide information about the general equation of state, and often have applications in geophysics and in shockwave experiments. The strain derivatives of the second-order elastic constants are related to the higher-order elastic constants which in turn are related to the anharmonicity of the lattice.

EXPERIMENTAL PROCEDURE

The RbCl, RbBr, and RbI crystals were bought from Semielements Inc. These crystals had been cut in the shape of half-inch cubes with orientations of (001), (110), or (111) (within 2°). The rubidium halide specimens from these crystals were prepared (i) by reducing the orientation uncertainty to less than $\pm 0.4^\circ$, (ii) by making the faces normal to this new orientation flat and parallel within $\pm 1'$, and (iii) by polishing these opposing faces. The methods by which the orientation uncertainties were reduced, etc., have been described elsewhere.¹ The specimen thicknesses were measured to an accuracy of ± 0.00025 cm.

Wave velocities in the specimens were measured by the ultrasonic-interferometry method originally developed by Williams and Lamb² and subsequently modified by Colvin.³ The method requires that a specimen is acoustically coupled to a transducer by a suitable cement. In the present work the specimens were coupled to quartz transducers of 10-MHz resonant frequency and 1.016 cm in diam with coaxial gold-coated electrodes. At temperatures below 300°K Nonaq stopcock grease served as cement. At 300°K Salol was used as the bonding agent. The maximum thickness of the bonding material was less than the margin of error in the measurement of the widths of the specimens, i.e., ± 0.00025 cm.

In the ultrasonic interferometry method, two phase-coherent rf pulses are sent in succession through the specimen. Each of these pulses generates its own train of echoes. These two echo trains are brought into temporal coincidence by varying the time delay between the two exciting pulses until destructive interference occurs as it does at certain discrete frequencies. These null frequencies were measured on a calibrated Beckman Universal Eput and Timer 8370A.

The physical arrangement used for the study of variation in the elastic constants of the three rubidium halides as a function of pressure and temperature is described in Refs. 1 and 4. However, in place of the manganin gauge used by previous researchers the pressure was measured on a calibrated Bourdon gauge and the temperature was measured by a copper-constantan thermocouple. Helium and argon were used as the pressure transmitting media. With this equipment the pressure could be held within ± 5 bars and the absolute accuracy of the temperature measurement was estimated to be $\pm 1^\circ\text{K}$.

We have in most cases measured four velocities since four specimens could be placed in the pressure vessel at the same time. In addition we have replicated a few experimental runs. Thus, we have made more than the minimally required number of independent velocity measurements to understand the elastic properties of cubic crystals. This permits an evaluation of the quality of measurements taken and hence of the validity of the results obtained from such measurements.

In general, null-frequency data was collected in the following way. The pressure bomb containing four specimens of one of the halides was allowed to attain thermal equilibrium at a specific temperature and pressure before any frequencies were recorded. Each such measurement consisted of recording five to six null frequencies for each velocity mode around the resonant frequency of the transducer. After measurement the pressure was raised slowly to a higher pressure and the system was allowed to come to thermal equilibrium before the next set of measurements was made. The

thermal equilibrium of the system at a specific pressure and temperature was inferred from the absence of drift in the value of a null frequency. The null-frequency measurements could be easily replicated within ± 0.5 kHz. Most of the measurements, at a specific temperature, were made in steps of 200 to 250 bars.

METHOD OF ANALYSIS OF NULL FREQUENCY DATA

A single transducer is used here both as the transmitter and the receiver of a signal in the ultrasonic interferometer of Williams and Lamb.² For destructive interference the phase difference between oscillations making up the two pulses must be an odd number times π radians. The difference in path comes from the fact that the first pulse makes one extra round trip and gets reflected one extra time at both sample surfaces. Hence

$$(2\pi f_n)2\tau - \phi - \pi = (2n-1)\pi. \quad (1)$$

Here f_n is the oscillator frequency at which the n th null occurs, and 2τ is the round-trip transit time of the pulse in the sample. The angle ϕ is the phase shift on reflection at the specimen surface which has a transducer and π is the phase shift at the free sample surface.

ϕ and n must be known, and the main problem is that of determining ϕ and n . This is accomplished by showing that ϕ , as a function of frequency f , is nearly linear near the resonant frequency, f_0 , of the transducer and the coupling film is assumed to have zero thickness.

The approximate values of ϕ in this case is given as^{2,5}

$$\phi = \pi \{ 1 - 2[(f_n - f_0)/f_0](Z_T/Z_S) \}, \quad (2)$$

where Z_T , the transducer impedance, is equal to the density multiplied by the sound velocity in the transducer and Z_S , the specimen impedance, is equal to the product of density times the sound velocity of the specimen. The evaluation of n is accomplished by combining Eqs. (1) and (2). Using the results for n and $n+1$, one can express the frequency difference $\Delta f_n = f_{n+1} - f_n$ between points of complete interference and again with Eq. (2), obtain the relation

$$n = (f_n/\Delta f_n) - (Z_T/Z_S) - 0.5. \quad (3)$$

Solving Eq. (1) for 2τ we get

$$2\tau = [(n+0.5)/f_n] - (Z_T/Z_S)[(f_n - f_0)/f_n f_0]. \quad (4)$$

From τ the velocity can finally be found

$$v = L/\tau, \quad (5)$$

where L is the length of the specimen. From Eq. (4) it is evident that the effect of Z_T/Z_S on τ becomes negligible near f_0 ; a transit time obtained near f_0 will not suffer from the effect of inaccurate knowledge of

Z_T/Z_S . The values of the resonant frequency of the transducer, f_0 , and the impedance of quartz at pressure and temperature are obtained from the work of McSkimin and Anderlecht.⁶

Cook's⁷ analysis of ultrasonic data is used in our calculation to measure the first pressure derivative of elastic constants of cubic crystals.

We have for the isothermal bulk modulus

$$B^T = -V(\partial P/\partial V)_T = -\frac{1}{3}L(\partial P/\partial L)_T \\ = \rho(\partial P/\partial \rho)_T = \frac{1}{3}\lambda(\partial P/\partial \lambda)_T, \quad (6)$$

where V is the volume, T is the temperature, L is length, ρ is density, and P is the pressure and

$$\lambda = L(P=0)/L(P), \quad (7)$$

here $L(P=0)$ and $L(P)$ are the length of the sample at pressure equal to zero and P , respectively. From thermodynamics the adiabatic bulk modulus is given by

$$B^S = B^T(1 + \Delta), \quad (8)$$

where

$$\Delta = \beta^2 B^S T / \rho C_P. \quad (9)$$

Here β is the volume-expansion coefficient and C_P is the heat capacity. Ultrasonically we have

$$C_{11}^S = \rho V l^2 = \rho [L_1^2(P)/\tau_1^2(P)] \\ = \rho_0 [L_1^2(P=0)/\tau_1^2(P)]\lambda, \quad (10)$$

where ρ_0 is the density at zero pressure and $\tau_1(P)$ is the transit time at pressure equal to P . We have

$$C' = (C_{11}^S - C_{12}^S)/2, \\ C'^S = C'^T = \rho_0 [L_2^2(P=0)/\tau_2^2(P)]\lambda. \quad (11)$$

We can write

$$B^S = C_{11}^S - \frac{4}{3}C' \\ = \rho_0 \left(\frac{L_1^2(P=0)}{\tau_1^2(P)} - \frac{4}{3} \frac{L_2^2(P=0)}{\tau_2^2(P)} \right) \lambda. \quad (12)$$

Using Eqs. (6), (8), and (12) we obtain

$$\rho_0 \left(\frac{L_1^2(P=0)}{\tau_1^2(P)} - \frac{4}{3} \frac{L_2^2(P=0)}{\tau_2^2(P)} \right) \lambda = \frac{1}{3}\lambda \left(\frac{\partial P}{\partial \lambda} \right)_T (1 + \Delta),$$

and after integration we have

$$\lambda = 1 + (3\rho_0)^{-1} \\ \times \int_0^P \frac{(1 + \Delta)dP}{[L_1^2(P=0)/\tau_1^2(P)] - \frac{4}{3}[L_2^2(P=0)/\tau_2^2(P)]}. \quad (13)$$

Since we know ρ_0 , $L_1(P=0)$ and $L_2(P=0)$ from zero pressure measurements and we measure $\tau_1(P)$ and $\tau_2(P)$ at P we would have $\lambda(P)$ at a given temperature if we had $\Delta(P)$ at that same temperature. Cook assumed at this point that $\Delta(P)$ is constant and may be approximately given by its value at one atmosphere. Ho