Elastic Constants of CsBr from 4.2°K to 300°K*

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Measurements of the elastic constants from 4.2°K to 300°K have been made on single crystals of cesium bromide. The values of the elastic constants at 4.2°K are $c_{11}=3.350\pm0.8\%$, $c_{12}=1.025\pm10\%$, and $c_{44}=1.002\pm0.8\%$ in units of 10^{11} dynes/cm². The Debye temperature (θ_0) at 0°K as calculated from the elastic constants is 149.0°K±2°K. The lattice energy at 0°K is computed to be $U_0=147.6$ kcal/mole.

INTRODUCTION

In recent years this laboratory has been using the echo-ranging method to measure the elastic constants of several alkali halides. Until now we have dealt only with the face-centered cubic (NaCl type) atomic structure.[1–3] However, in the present work we have begun a study of the body-centered cubic (CsCl type) atomic structure. W. Ludwig of Technische Hochschule, Aachen has pointed out to us that the usual theoretical models (central forces, Born-Mayer-replusion) indicates that these constants for the CsCl type of structure should have nearly the same temperature dependence as the NaCl type structure but that c_{11} should be less temperature dependent for the CsCl type. We shall see that this is experimentally verified for c_{11} but not for c_{44}.

EXPERIMENTAL

The single-crystal specimen used for these measurements was obtained from Harshaw Chemical Company and is of the high purity, optically clear type supplied by that company. Only one specimen was used for all measurements. The specimen was obtained as a cube of $1\frac{1}{4}$ inch on a side. Orientation of the crystalline planes within the specimen was then obtained by the Laue x-ray back reflection method.[4] Two surfaces were ground parallel to the (100) crystalline planes. Another pair of surfaces were ground parallel to the (110) crystalline planes. The path length between both pairs of the parallel ground surfaces was approximately 2.7 cm.

To obtain the adiabatic elastic constants we have used the echo-time method. To obtain the constants c_{11} and c_{44} one simply measures the velocity (v) of 10-Mc/sec longitudinal and transverse waves propagated in the [100] direction. If the density ρ is known, the following relations may be used: $c_{11}=\rho v_L^2$ and $c_{44}=\rho v_T^2$. To obtain c_{12} one measures the velocity of longitudinal waves along the [110] direction for which $c_{12}=2\rho v_L^2-(c_{11}+2c_{44})$. The technique for measuring the velocity of sound in CsBr was similar to that discussed by Norwood and Briscoe.[2] Transverse waves traveling in the [110] direction could also have been used to determine the elastic constants. However, since the polarization of particle motion must be known this procedure is more difficult.

The adhesive seal between the quartz transducer and the sample was phenyl salicylate (Salol) for the temperature range of 300°K to 220°K. Below 60°K the binder was solid natural gas. For measurements between 110°K and 60°K the binder was an organic mixture of ethyl ether, ethyl alcohol, and isopentane.

The temperature was measured with a copper-constantan thermocouple which was in contact with the specimen.

RESULTS

The values of the elastic constants are given in Table I. Also included in this table are the compressibilities calculated from the equation for cubic crystals, $\beta=3/(c_{11}+2c_{12})$. Figure 1 is a plot of the elastic constants vs temperature. Due to the linearity of other alkali halides in the temperature range of 220°K to 50°K, we felt that an interpolation would be sufficient. There are data[5] available on the density at 0°C. There are data available on the expansion coefficients from

TABLE I. Elastic constants in units of 10^{11} dynes/cm² and compressibilities in units of 10^{-12} cm²/dyne as a function of temperature (°K) for cesium bromide.

T	c_{11}	c_{12}	c_{44}	β
300	3.056	0.776	0.743	6.510
280	3.071	0.818	0.759	6.373
260	3.091	0.845	0.775	6.275
240	3.111	0.852	0.792	6.231
220	3.137	0.866	0.809	6.161
110			0.913	
90			0.935	
70			0.956	
50	3.311	1.014	0.976	5.619
40	3.316	1.015	0.984	5.612
30	3.323	1.024	0.992	5.586
20	3.334	1.025	0.997	5.572
10	3.347	1.022	1.001	5.565
4.2	3.350	1.025	1.002	5.556

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300°K to 134°K.[6] There are no data available on the specific heat of CsBr. However, to obtain the expansion coefficient from 134°K to 0°K we used the Grüneisen relationship using an estimated shape of the specific heat curve modeled after that of other alkali halides.[7] (The error involved in this procedure is negligible.) The densities to 0°K were then calculated from the derived expansion coefficient. The total change in length of the specimen betwen 300°K and 4.2°K was approximately 1.0%. The change of density was approximately 3.1%. Binder corrections of 0.04 μsec for transverse and 0.03 μsec for longitudinal waves[8] were subtracted from the observed delay times. The estimated errors at 4.2°K for c_{11}, c_{12}, and c_{44} are $\pm 0.8\%$, $\pm 10\%$, and $+0.8\%$, respectively.

Work on the elastic constants of CsBr has been presented at meetings of the American Physical Society. Bolef and Menes[9] gave room temperature values of $c_{11}=3.00\pm 0.8\%$, $c_{44}=0.75\pm 0.8\%$, and $c_{12}=0.78\pm 8\%$. Reinitz and Huntington[10] gave values at 295°K of $c_{11}=3.097$, $c_{44}=0.75$, and $c_{12}=0.903$, all in units of 10^{11} dynes/cm^2. Kirshnan and Roy,[11] using a central force model, calculated theoretical values of the elastic constants of CsBr at 0°K. They obtained values of $c_{11}=3.5$ and $c_{44}=c_{12}=0.6$ in units of 10^{11} dynes/cm^2. The Cauchy relation at 0°K ($c_{12}=c_{44}$), which is predicted by this particular theoretical model, appears to find some verification in our results. It should be remembered, however, that the possible error of c_{12} is quite large.

The Debye temperature at 0°K (θ_0) has been calculated from the elastic constants. Using the Betts, Bhatia, and Wyman method,[12] we obtained a value of 149.2°K±2°K. Using De Launay's tables,[13] a value of 149.0°K±2°K was obtained. Based on earlier work with the alkali halides,[1–3] we predict that the Debye temperature computed from specific heat data on CsBr at temperatures below 3°K will be within 1% of our value of $\theta_0=149$°K.

DISCUSSION

Let us reflect now on the information which we have available concerning the face- and body-centered cubic structures. If we consider the temperature dependence of the elastic constants in cooling from 300°K to 4.2°K, we find the following: for the face-centered cubic (with the exception of (CaF_2) $\Delta c_{11}\cong 20\%$ and $\Delta c_{44}\cong 5\%$. For the body centered cubic $\Delta c_{11}\cong 10\%$ and $\Delta c_{44}\cong 30\%$. We see that Δc_{11} does vary as predicted in the introduction; however, Δc_{44} varies quite contrary to the prediction. It should also be pointed out that Δc_{12} for the body-centered has a positive slope whereas for the face centered this slope is negative. These results appear to pose an interesting theoretical problem.

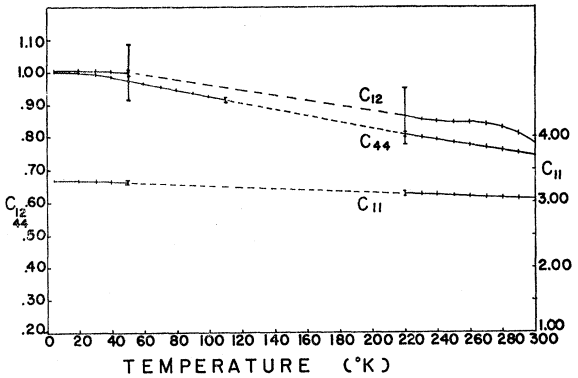

FIG. 1. Elastic constants of cesium bromide in units of 10^{11} dynes/cm^2.

The compressibility, which we have calculated from the elastic constants at 4.2°K, was used to calculate the lattice energy[14] for CsBr. Using[14] for the Madelung constant $\alpha=1.762670$, we obtain $U_0=147.6$ kcal/mole. This may be compared to the experimental value[14] of 148.6 kcal/mole.

An interesting relationship was found to exist for the velocity of compressional waves in the [100] direction and the [110] direction. If we consider the face-centered cubic KCl, which has an ionic radii ratio near to that of CsBr, we find the percentage variation of the velocity along the two directions at 4.2°K to be $\Delta v_L\cong 18\%$ for KCl and $\Delta v_L\cong 2.6\%$ for CsBr. This appears to indicate that the potential well in which an ion is located is more symmetrical for the body-centered than for the face-centered cubic. This does not necessarily hold true for the case of a large ionic radii ratio where there can exist an electron cloud shielding.

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