

Fig. 2. Compression of RbF. ○ increasing pressure, ● decreasing pressure, ---- smoothed data of Vaidya and Kennedy[1], — (upper curve) calculated by eqn (1) using ultrasonic parameters, (lower curve eqn (1) using least squares fit to data.

those of Vaidya and Kennedy (also plotted in Fig. 2) in that no low pressure (10 kbar) transition was seen and the higher transition occurred with a much larger volume change than they reported although the pressure of this transition was in good agreement. We again suggest that their sample was contaminated with moisture. A calculation using the ultrasonically determined data of Roberts and Smith[6] in the Birch-Murnaghan equation is shown in Fig. 2 as the solid line passes through our data for B1 in excellent agreement. A least squares fit to the data on the B2 phase is also shown in that figure.

In fitting the Birch-Murnaghan equation to the data on the B2 phase of RbF, we have followed a procedure which is more complicated than has usually been used for the reduction of equation of state data, although the technique has been known for some time[16]. Briefly, a computer program was used to choose equation of state parameters which minimize

$$\chi^2 = \sum_i \left( \frac{P_i - P_{\text{calc}i}}{\sigma_{P_i}} \right)^2 + \left( \frac{V_i - V_{\text{calc}i}}{\sigma_{V_i}} \right)^2. \quad (2)$$

Here  $P_i$ ,  $V_i$ ,  $\sigma_{P_i}$  and  $\sigma_{V_i}$  are the measured pressure and volume and their standard deviation for each data point.  $P_{\text{calc}i}$  and  $V_{\text{calc}i}$  are the calculated pressure and volume corresponding to this data point. In the usual least squares procedure only one of the terms inside the summation in (2) is used. However in the present case when errors in both  $P$  and  $V$  are important the present method gives a more accurate value for derived equation of state parameters and especially for the calculated standard deviation of these parameters.

The data for RbF is not sufficient to permit an accurate determination of  $K'_0$  and so we have assumed  $K'_0 = 5.0$  and used the least squares procedure to estimate  $V_0$  and  $K_0$ . The derived values are  $V_0(\text{B2})/V_0(\text{B1}) = 0.870 \pm 0.003$  and  $K_0 = 315 \pm 11$  kbar. The calculated  $\Delta V/V_0(\text{B1})$  at the transition pressure is 0.111.

#### 4. DISCUSSION

In the course of high pressure research, we often want to make predictions of high pressure polymorphism. While the applicable theories are necessarily crude, they are nevertheless useful in the identification of high pressure phases when the data on the high pressure phase is incomplete. These theories provide clues of possible polymorphism in areas of interest where present experimental data is sparse, such as the regime of the earth's deep interior. These theories are also of particular utility in choosing fertile regions for future high pressure experimentation.

The alkali halides are particularly useful for testing this sort of theory. The present correction to the current knowledge of compression and phase changes in alkali-halides removes a serious source of previous misinterpretation. Accurate information on the B1-B2 phase transition is now available for 9 alkali halides (NaCl and the potassium and rubidium halides). Less accurate data is available for two more (NaF and CsF) while the remaining 6 B1 type alkali halides have no known high pressure transition. There is also information on the high temperature B2→B1 transition in CsCl. We were particularly eager to incorporate the present data in a test of two theories we have found useful in predicting high pressure polymorphism.

Jamieson[17] has recently shown how considerations based on ionic radius ratios could be useful in determination of available crystal structures for high pressure phase transformations. Figure 3 shows graphically the relative volume change at the B1-B2 transition for 12 compounds, as a function of the cation-anion radius ratio,  $r_a/r_x$ . The ionic radii  $r_a$  and  $r_x$  are taken from Shannon[20]. The values for the relative volume change at the transition were mostly taken from Bassett and Takahashi[22]. The NaF volume change is from shock wave experiments of Carter[11]. We have omitted the Weir and Piermarini[3] data on CsF on the grounds of a probable pressure distribution across their sample as discussed before for KF and RbF. The AgF data is from Jamieson *et al.*[23]. The data on KF and RbF is from the present study.

A hard sphere ion model predicts a 23% volume

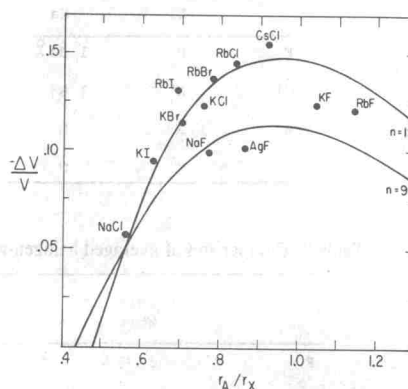


Fig. 3.  $\Delta V/V$  vs radius ratio  $r_a/r_x$  (six coordination) for the B1→B2 high pressure phase transition for alkali halides. ○ Experimental data, — calculated from ionic model with power law repulsion,  $b/r^n$ .



change for the B1-B2 transition when the radius ratio lies between 0.7 and 1.4. A more reasonable assumption is that the ions are repelled by a force having the form  $b/r^n$ , and that the relative strength of the anion-cation, cation-cation, and anion-anion forces depends upon the radius ratio. Such a model has been proposed by Pauling[21] and we have used it to calculate the volume change for the B1-B2 transition for various values of the repulsive parameter  $n$ . These curves are in good qualitative agreement with the data. The new KF and RbF data points are the only points for radius ratios greater than one. They tend to confirm the theoretical curves which peak at a radius ratio of about 0.9.

The important conclusion from Fig. 3 is that B1 structure compounds with radius ratios less than about 0.5 are not expected to transform to the B2 structure at high pressure because the volume change is positive. Thus LiF ( $r_a/r_x = 0.57$ ) and the B1 oxides CaO ( $r_a/r_x = 0.71$ ), SrO ( $r_a/r_x = 0.84$ ), and BaO ( $r_a/r_x = 0.96$ ) may transform to the B2 structure at high pressure. (Carter[11] does report a possible transition in LiF around 900 kbar.) In FeO ( $r_a/r_x = 0.56$ ), we could ordinarily expect a high pressure transition. However an electronic transition in iron from high spin to low spin may occur. For low spin FeO  $r_a/r_x = 0.40$ , so we suspect that a high pressure B1-B2 transition may or may not occur for this compound. The situation is unclear for NaBr ( $r_a/r_x = 0.52$ ), NaI ( $r_a/r_x = 0.46$ ) and MgO ( $r_a/r_x = 0.51$ ). LiCl, LiBr and LiI are *not* expected to transform to the B2 structure.

Since the  $\Delta V/V$  of these B1-B2 transitions seem to be well correlated in terms of their radius ratios, we can estimate the radius of halogen anions in eight coordination which has not been done for recent tabulations of ionic radii, e.g. Shannon[20] where only their six coordinated radii are given. To do this we assume radii are additive and then from a hard sphere model, using  $\Delta V/V$  at pressure from Fig. 3 and Shannon's (1 bar) six coordinated radii we obtain Table 1. If the model were perfect there would be equality along each row. We note that the eight coordinated radii range from equal for  $F^-$

to 2% greater for  $I^-$  than the six coordinated radii (AgF, not tabulated in the B2 phase, gives  $F^-$  equal to 1.33 Å).

To test approach further, Table 2 displays halogen-radii in eight coordination using averages from Table 1; those calculated from interatomic spacings given by Schulz[24] for NaCl types obtained from normally CsCl salts evaporated on several substrates and also values calculated from Cs-halogen cell edges at 25°C from NBS Circular 539[25]. The calculation was done using Schulz's difference in interatomic distance combined with Shannon's[20]  $r_6$ . Schulz's quoted error was  $\pm 0.02$  Å. The agreement for the two types of coexisting phases is excellent and well within the combined experimental error. Even the agreement with the calculated room temperature values is excellent when it is remembered that strictly speaking these ionic radii are not additive to give actual cell edges (Shannon[20]). We also note that the  $r_8/r_6$  ratio is slightly variable reaching 3% only for  $I^-$  and that  $F^-$  is constant as might be intuitively expected.

Demarest[26, 27] has recently proposed a modification of the Born stability criterion for the prediction of high pressure polymorphic transitions. The Born stability criterion is based on the fact that a crystal lattice is unstable when one of the eigenvalues of the elastic constant matrix is negative. The eigenvalue of interest in this case is equal to the shear elastic constant  $C_{44}$ . In fact experimental measurements on a number of alkali halides under pressure have shown that  $C_{44}$  often decreases with pressure[5, 6], in contrast to the increase found for most crystals, and the extrapolation of this decrease to the pressure where  $C_{44} = 0$  has often been used to place limits on the B1-B2 transition pressure. However in nearly all cases a phase transition takes place at much lower pressures than predicted by this method.

The modified Born criterion predicts a phase transition to occur whenever the ratio of the critical eigenvalue (here,  $C_{44}$ ) to the bulk modulus reaches a critical value,  $\alpha = C_{44}/K$  at the transition. According this theory  $\alpha$  depends primarily on the geometrical details of the transformation. The theoretical justification for this type

Table 1. 8-Coordinated radii ( $r_8$ ) for halogen-ions  $X^-$  means transition impossible,  $U$  means unstudied phase

	Li	Na	K	Rb	Cs	$r_6$
F	U	1.30 Å	1.32	1.37	U	1.33
Cl	X	1.85	1.82	1.84	1.85	1.81
Br	X	U	1.99	2.01	U	1.96
I	X	U	2.27	2.26	U	2.20

Table 2. Comparison of averaged halogen-ions from Table 1 with those calculated in alternate fashions

	This Work	NBS [25]	Schulz [24] $C_8$	Tl
F	1.33 Å	----	-----	----
Cl	1.84	1.83	1.855	1.900
Br	2.00	1.98	2.01	2.04
I	2.27	2.22	2.26	2.29