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THE HIGH PRESSURE PHASE TRANSITIONS IN KF AND RbF

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Abstract—The high pressure B1 ↔ B2 transitions in KF at ~ 40 kbar and RbF at ~ 30 kbar have been studied using hydrostatic X-ray diffraction. No other transitions have been observed. The addition of the $\Delta V/V$ for these transitions to the already existing body of literature on B1–B2 transitions in alkali halides permits an extension of Pauling's theory to larger values of radius ratios. It also permits the modified Born criterion for predicting phase transitions to be further verified. Values of ionic radii for 8 coordination we suggest are 1.33 Å for F^-, 1.84 Å for Cl^-, 2.00 Å for Br^- and 2.27 Å for I^-.

1. INTRODUCTION

In the past, there has been great interest in the compression of solids and in polymorphic phase transitions under pressure. There has been particular interest in the alkali halides, because they serve as typical examples of ionic crystals, and because they can serve as a test of models of the compressibility and phase transitions of ionic solids.

Vaidya and Kennedy[1] have recently presented a comprehensive experimental study of the compression of all (except CsF) alkali halides to 45 kbar (1 kbar = 0.1 GPa) at room temperature in a piston cylinder device. In most cases, their results are in excellent agreement with other work. However we noticed discrepancies in their data for KF and RbF. Vaidya and Kennedy report a phase transition in KF at 17.8 kbar and two in RbF at 12 and 30 kbar. Darnell and McCollum[2] also using a piston cylinder report no transition in KF to 45 kbar and a single transition in RbF at 34 kbar. Weir and Piermarini[3] in their diamond anvil X-ray work had earlier reported the expected B1 (NaCl type) to B2 (CsCl type) transition in KF at ~ 35 kbar and RbF at ~ 12 kbar. The reported volume changes in these three experiments were not in agreement. More recently, Morris and Jamieson[4], in a study of elastic wave velocities in these and other alkali halides found a transition in KF at about 40 kbar and in RbF at about 30 kbar. Finally, the compressibility of the low pressure phase of RbF and KF reported by Vaidya and Kennedy is not in agreement with that derived from ultrasonic experiments[5, 6].

Since the high pressure behavior of alkali–halides is of considerable theoretical interest it seemed wise to repeat the study of these two compounds under pressure using X-ray diffraction so as to have positive phase identification and determine the compressibility of the high pressure phases, using a modern modern and improved X-ray technique. Very shortly after this study was inaugurated we received from the author Yagi[7] a report of his own study on KF, however we thought it advisable to continue our work on this substance as our pressure generating techniques were quite different.

2. EXPERIMENTAL METHOD

We used a Jamieson–Lawson high pressure X-ray 114.7 mm powder diffraction camera as modified by Halleck and Olinger[8] using monochromatized Cu-target radiation. The pressure cell was a Be disc 0.30 mm thick with a 0.30 mm hole at its center. The sample was placed in this hole together with a hydrostatic fluid. Due to probable reactivity of these extremely hydroscopic fluorides with the usual methanol–ethanol pressure fluid we used a 1 : 1 pentane–isopentane mixture, which remains hydrostatic to about 70 kbar[9]. The disc assembly is pressurized between carbide pistons in the center of the cylindrical film holder. Due to the tendency of RbF and KF to form hydrates by the absorption of water vapor from the air, all sample preparation was performed in a (dried) nitrogen dry box. Samples were 99.9% pure. The KF sample was provided by C. E. Morris at Los Alamos. The RbF was purchased from Alfa Chemical Company. Samples were ground with a mortar and pestel, passed through a 320 mesh sieve, and usually mixed with a similarly prepared pressure standard (NaF). A teflon retaining ring (dam) placed around the lower carbide piston permitted the sample to be inundated with the exceedingly volatile pressure fluid while it and the camera assembly were transported from the dry box to the press. The dam was slid back after pressure was applied. Exposure times were typically three days.

In spite of our care, we were often unsuccessful in loading the desired material into the cell, and our present technique of loading evolved from the failure of earlier attempts. Even using the above procedure, we occasionally found that our samples had reacted with water vapor to form a hydrate. On two occasions, our sample reacted with the pressure standard which was mixed with the sample. On one occasion KF and NaCl in the presence of a 4 : 1 methanol–ethanol pressure fluid reacted to form KCl and NaF. On another occasion a sample of LiBr reacted with our NaF pressure standard in the presence of a pentane/isopentane pressure fluid to form NaBr. On other runs under what we thought were identical conditions the LiBr did not react with the NaF. Tabulated thermochemical data[10] confirms that both of these reactions can occur under ambient conditions. However we find the reaction in the presence of pentane/isopentane, in which we believe alkali halides are insoluble, to be particularly puzzling. Our experience shows that sample reactivity can place restraints upon the choice of pressure standards and pressure fluids in this type of experiment.

In most runs NaF was mixed with the sample, and the pressure was determined from a tabulation [Olinger, private communication, 1977] based on a reduction of raw shock wave data to an isotherm. This tabulation is a minor revision of the tabulation of Carter[11]. Within experimental error, this NaF pressure scale is equivalent to the one proposed by Spieglan and Jamieson[12] which involves conversion of NaF compression to NaCl compression and the use of the Fritz *et al.*[13], NaCl pressure scale.

Typically, three or more *d* spacings (111, 200 and 220 for the B1, 100, 110 and 111 for the B2 phase) were measured for each exposure. A standard deviation for each *d* spacing was calculated from our ability to measure the peak position of a diffraction line to 0.15 mm (one standard deviation; 1 mm = 1° on our camera). Weighted average values and weighted standard deviations for the lattice parameters were calculated by the usual formulas (e.g. Meyer[14], eqns 10.4h and 10.4i). Typically our calculated lattice parameters had a standard deviation of 0.04% leading to a standard deviation of about 0.12% in the relative volume V/V_0 and a standard deviation of about 1 kbar in the pressure calculated from the NaF pressure scale. χ^2 tests on over 100 lattice parameter measurements show that our accuracy is actually a little better than this. Film shrinkage was measured and corrected for on each film by fiducial shadows cast by the camera.

3. RESULTS

Two successful runs were made on KF. In one, no internal pressure standard was used. Instead pressure was estimated using the bulk modulus K_0 and its derivative K_0' of KF at 1 bar from Roberts and Smith[5] in the Birch–Murnaghan equation of state

$$P/K_0 = (V_0/V)^{5/3}[\eta + (K_0' - 4)\eta^3], \quad \eta = 3/2[(V_0/V)^{2/3} - 1] \qquad (1)$$

for the B1 phase, and Yagi's[7] compression data for points in the B2 phase. Our second successful run included NaF as a pressure standard. Yagi[7] used a Decker[15] NaCl equation of state which stems from a lattice model combined with 1 bar experimental data. At 40 kbar this Decker scale is about 1 kbar lower in pressure for a given NaCl compression than the scale we used. Hence for a comparison of the data on the *same* pressure scale the Yagi points should be raised 1 kbar at 40 kbar (or conversely for ours). This has been done in Fig. 1 where we present also our own results, those of Vaidya and Kennedy, and the extrapolation of the Birch–Murnaghan equation based on the ultrasonic values of K_0 and K_0' from [5]. There it can be seen that the pressures calculated from K_0 and K_0' values at 1 bar give compressions as valid as those from an internal NaF standard.

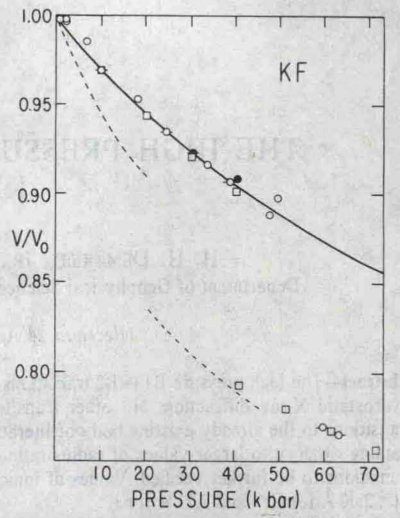

Fig. 1. Compression of KF. ○ our data, increasing pressure, ● our data, decreasing pressure, —○— our data, no internal pressure standard, □ Yagi's[7] data, ----- smoothed data of Vaidya and Kennedy[1], —— calculated by eqn (1) using ultrasonic parameters.

It can be seen that our own experiment is in good agreement with Yagi's data and with the Birch–Murnaghan equation. Vaidya and Kennedy's data is in disagreement. We believe that their sample may have become contaminated with water, and that their curve represents the compression and phase changes of such a contaminated sample. Yagi reported[7] no hysteresis in the B1–B2 transition in his quasi-hydrostatic study. In our truly hydrostatic study hysteresis was extensive, the B1 phase persisted to about 49 kbar on pressure increase while the back B2–B1 ran more in the neighborhood of 32 kbar. Yagi[7] and Morris and Jamieson[4] both report a sharp inaugeration of the transition at 38–40 kbar and both studies used non hydrostatic media. When the data of Weir and Piermarini[3] are assigned a pressure using the Yagi data it is apparent that their pattern was taken at ~ 75 kbar rather than their quoted circa 35 kbar which stemmed from a force/area estimate of pressure. It is obvious that they had a strong pressure gradient across their sample as the "coexisting" B1 phase had a lattice parameter corresponding to a compression of 0.992 or a pressure of ~ 3 kbar. It seems certain that their B2 phase was surrounded by a rim of B1 in their ungasketed technique.

One successful run was made on RbF. The results are illustrated in Fig. 2. The B2 phase first appeared at 33 kbar in good agreement with the 30 kbar of Morris and Jamieson[4] but in disagreement with Weir and Piermarini[3]. Using our compression data with the lattice parameters of Weir and Piermarini, we obtain values of 2 kbar for the B1 phase and 38 kbar for the B2 in their experiment. The explanation for this disagreement seems to be the same as for the KF discrepancy, i.e. strong pressure gradients across their sample. Our results are in marked disagreement with

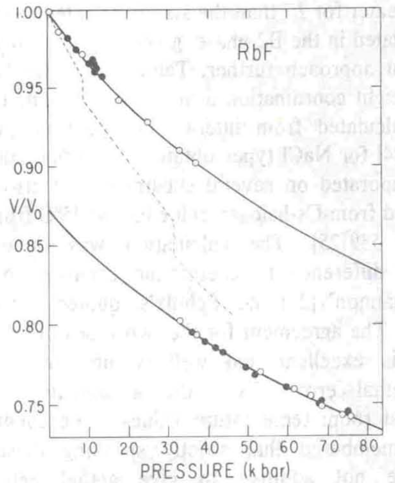

Fig. 2. Compression of RbF. ○ increasing pressure, ● decreasing pressure, ----- smoothed data of Vaidya and Kennedy[1], —— (upper curve) calculated by eqn (1) using ultrasonic parameters, (lower curve eqn (1) using least squares fit to data.

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

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

Here P_i, V_i, σ_{pi} and σ_{Vi} are the measured pressure and volume and their standard deviation for each data point. P_{calc_i} and V_{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 parmeters 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

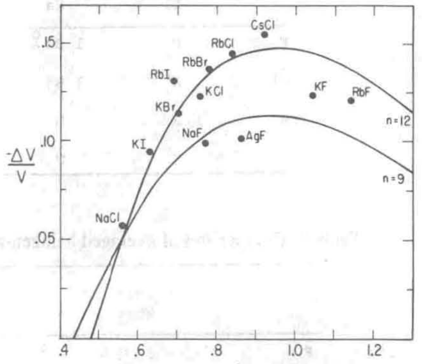

Fig. 3. $\Delta V/V$ vs radius ratio r_a/r_x (six coordination) for the B1→B2 high pressure phase transition for alkali halides. ○ Experimental data, —— calculated from ionic model with power law repulsion, b/r^n.

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 radio 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 ± 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 pase 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 α 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	C_s	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_s	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

of relationship is that the two polymorphic crystal structures may be related by a simple deformation. An elastic constant or a combination of them will be a measure of the mechanical resistance of the crystal to this deformation and the ratio of this elastic constant to the bulk modulus provides a suitable scaled measure of this mechanical resistance to deformation, and is also related to the free energy difference between the two phases, because this elastic constant is the second derivative of the free energy along a path connecting the two crystal structures.

Demarest *et al.*[27] showed that the idea of a modified Born criterion to predict phase transitions was consistent with a large body of data on phase transformations in various crystal structures. The data on KF and RbF appeared to be anomalous, however, because the transition pressures reported by Vaidya and Kennedy implied that $\alpha = 0.26$ and 0.28 for these two compounds, while for the other alkali–halides it ranged from 0.14 to 0.22. The revised values we get using the transition pressures reported in this paper are $\alpha = 0.19$ and 0.13 for KF and RbF, respectively.

The new data on the phase transitions in KF and RbF combined with the other data on transitions in alkali halides shows that the simple theories discussed here are in moderately good agreement with the data. This tends to confirm that this type of simple theory can be useful in predicting high pressure phase transitions in other systems which have not been so thoroughly studied by experiments.

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