

THE HIGH PRESSURE PHASE TRANSITIONS IN KF AND RbF

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Abstract—The high pressure B1 \leftrightarrow B2 transitions in KF at \sim 40 kbar and RbF at \sim 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 \sim 35 kbar and RbF at \sim 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 hygroscopic 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 pestle, 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 Spiegman 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

$$P/K_0 = (V_0/V)^{5/3}[\eta + (K'_0 - 4)\eta^3], \quad \eta = 3/2[(V_0/V)^{2/3} - 1] \quad (1)$$

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

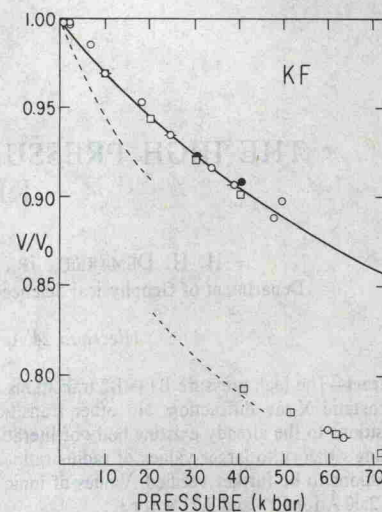


Fig. 1. Compression of KF. \circ our data, increasing pressure, \bullet our data, decreasing pressure, \circ — \circ our data, no internal pressure standard, \square Yagi's[7] data, ----- smoothed data of Vaidya and Kennedy[1], ——— calculated by eqn (1) using ultrasonic parameters.

compressions as valid as those from an internal NaF standard.

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 inauguration 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