

## THERMODYNAMICS OF THE $Fm3m \rightleftharpoons Pm3m$ TRANSITION IN THE POTASSIUM AND RUBIDIUM HALIDES\*

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**Abstract**—The  $Fm3m \rightleftharpoons Pm3m$  phase transition in the potassium and rubidium halides has been examined by a dilatometric method from 25°C to temperatures near the melting point. The pressure ( $P_{tr}$ ) and volume change ( $\Delta V_{tr}$ ) measured for these polymorphic transitions were treated by method of least squares. Averages of  $P_{tr}$  and  $\Delta V_{tr}$  at 25° were taken from this work and from data in the literature. These average values of  $P_{tr}$  and  $\Delta V_{tr}$  were used to calculate the  $P\Delta V$  work for this transition; the entropy change ( $\Delta S_{tr}$ ) was calculated from the average value of  $\Delta V_{tr}$  and the temperature coefficient, ( $dP_{tr}/dT$ ). Data are also given for  $P_{tr}$ ,  $\Delta V_{tr}$  and  $\Delta S_{tr}$  at the triple point ( $Fm3m \rightleftharpoons liquid \rightleftharpoons Pm3m$ ). No solid–solid transition was observed in KF below 800°C and 45 kb. The following trends are noted. At constant pressure, the entropy change  $\Delta S$  ( $Fm3m \rightarrow Pm3m$ ) is positive for the potassium salts KCl, KBr and KI; for the rubidium halides it is negative. The transition volume  $\Delta V$  ( $Fm3m \rightarrow Pm3m$ ) in all cases decreases as the temperature increases.

### 1. INTRODUCTION

THERE HAVE been numerous investigations of the pressure-induced polymorphic transition in the alkali halides since a transition of this type was first discovered in the rubidium halides RbBr and RbI by Slater[1] in 1926. Bridgman found a similar transition in RbCl [2] and in the potassium salts KCl, KBr and KI[3]. Piermarini and Weir[4, 5] also reported the discovery of a solid–solid transition in the fluorides, RbF and KF. Jacobs[6] established, by high pressure X-ray diffraction, that the pressure-induced phase transition in RbI is from the sodium chloride type structure (space group  $Fm3m$ ) to the denser cesium chloride type structure (space group  $Pm3m$ ). Other workers[5, 7–9] have shown that this same type of structure change also occurs in RbCl, RbBr, KI and KCl. A recent report by Klement and Jayaraman[10] summarizes the work which has been carried out on the phase transitions in these salts.

Most of the measurements of the poly-

morphic transition in these salts have been made at room temperature with the exception of the work by Bridgman[3], Pistorius[11, 12] and Pistorius and Snyman[13] at temperatures up to 200°C. We have studied the transition in the potassium and rubidium halides at higher temperatures by the volume discontinuity method[14, 15] to temperatures approaching the triple point between the two solid phases and the liquid phase. Data for the transition pressure ( $P_{tr}$ ), the transition volume ( $V_{tr}$ ) and their variation with temperature have been obtained and thermodynamic data were derived from these experimentally measured quantities. These will be presented and discussed in this paper.

### 2. EXPERIMENTAL

#### (A) Materials

The salts used in these measurements were Mallinckrodt analytical reagent grade with the exception of RbF which was obtained from the A. D. McKay Co. The fluorides, KF and RbF were dried at 300°C under vacuum ( $P < 10^{-6}$  Torr.) for 48 hr. This was followed by treatment with anhydrous HF at a pressure of 1 atm for 24 hr. The chlorides, bromides and iodides of these alkali metals were heated for 24 hr under high vacuum at a temperature of 150°C. The dried salts were compressed into pellets at a pressure of  $\sim 2$  kb. The fluorides, KF and RbF, were

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handled in an atmosphere of argon in order to reduce pickup of water.

### (B) Apparatus

Use of the piston displacement method for the detection of phase transitions has been described by Bridgman [14], Kennedy and Newton [15], and by Jayaraman *et al.* [16]. Our techniques are similar to those described by the above workers. However, we have extended the temperature range of this piston displacement method from the upper limit of  $\sim 200^\circ\text{C}$ , imposed by external heating of the compound cylinder apparatus, to temperatures of  $\sim 1000^\circ\text{C}$  which are attainable with use of the internally heated graphite furnace. In this modification the sample in the form of a cylinder 0.6 cm in dia. by 1.5 cm in length was placed within a cylindrical graphite furnace heating element within the high pressure chamber. The volume of the sample in this case now comprises approximately 20 per cent of the total volume of the pressure chamber.

The transition volume was determined by the piston displacement method. This technique has been used by Bridgman [14] and more recently described by Jayaraman *et al.* [17]. Usually the sample and piston have the same diameter; however, in the technique used here the sample and piston differ in diameter by a factor of two. Thus the sample and internal furnace apparatus must distort or 'flow' in order that the volume change which takes place in the sample be transmitted into a displacement of the piston. The greater reproducibility of the  $\Delta V_{tr}$  measure-

ments at higher temperatures, i.e.  $t > 200^\circ\text{C}$ , is very probably due to the increase in the plasticity of the furnace parts and of the sample at these higher temperatures.

For pressure calibration the phase transition  $\text{Bi(I)} \rightleftharpoons \text{Bi(II)}$  and  $\text{Bi(II)} \rightleftharpoons \text{Bi(III)}$  at  $25^\circ\text{C}$  were used. We find  $25.6 \pm 0.2$  kb and  $27.3 \pm 0.2$  kb respectively for these transitions. Kennedy and LaMori [18, 19] give  $25.38 \pm 0.02$  kb and  $27.0 \pm 0.2$  kb for these transitions in Bi at  $25^\circ\text{C}$ . It was assumed that this calibration holds good at higher temperatures also.

Temperatures were measured with a chromel-alumel thermocouple whose junction was positioned in the geometric center of the salt sample. No corrections for the pressure effect on e.m.f. were made since corrections at pressures below 25 kb are expected to be small, i.e. less than 1% for Cr-Al thermocouples [20].

### 3. RESULTS AND DISCUSSION

The pressures of this polymorphic transition ( $P_{tr}$ ) were determined upon compression and decompression at approximately  $100^\circ$  intervals, from 25 to  $700^\circ\text{C}$  and in some cases up to  $800^\circ\text{C}$ . The results for the salts KCl, KBr and KI are shown in Fig. 1; similarly, results for RbF, RbCl, RbBr and RbI are given in Fig. 2. No phase transition was ob-

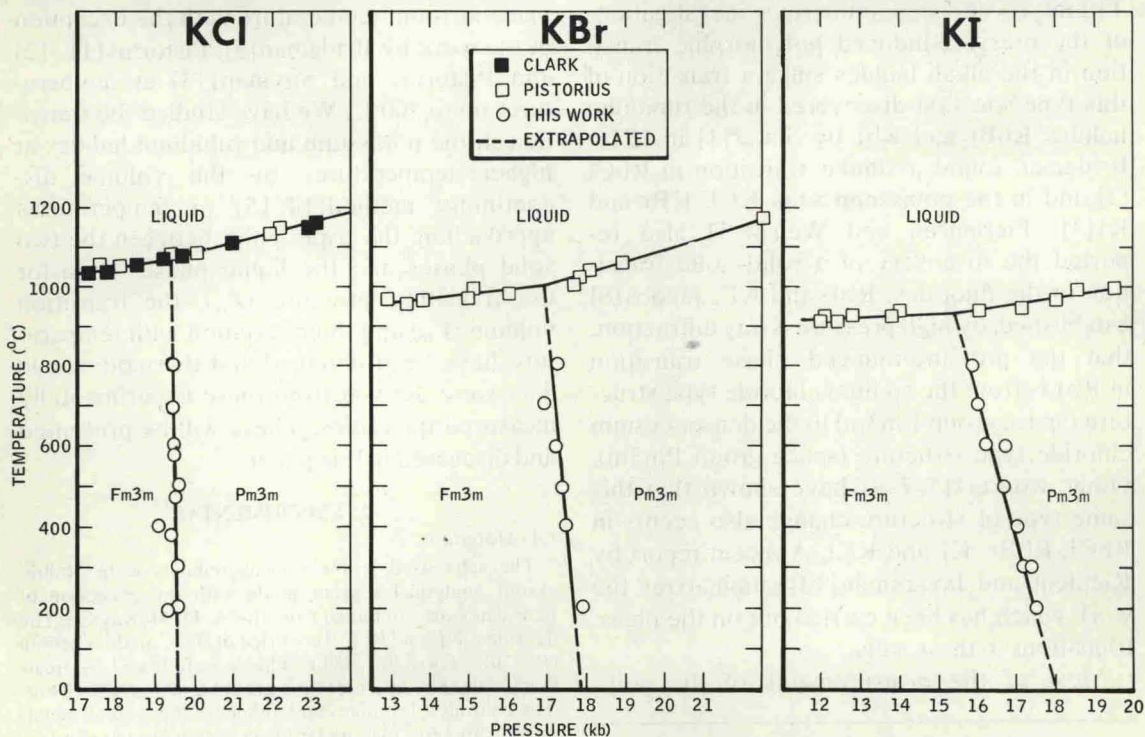


Fig. 1.  $PV$  diagram for the potassium halides KCl, KBr and KI: ■—melting point data of Clark (1959), □—melting point data of Pistorius (1965, 1966), ○— $\text{Fm3m} \rightleftharpoons \text{Pm3m}$  transition, this work.

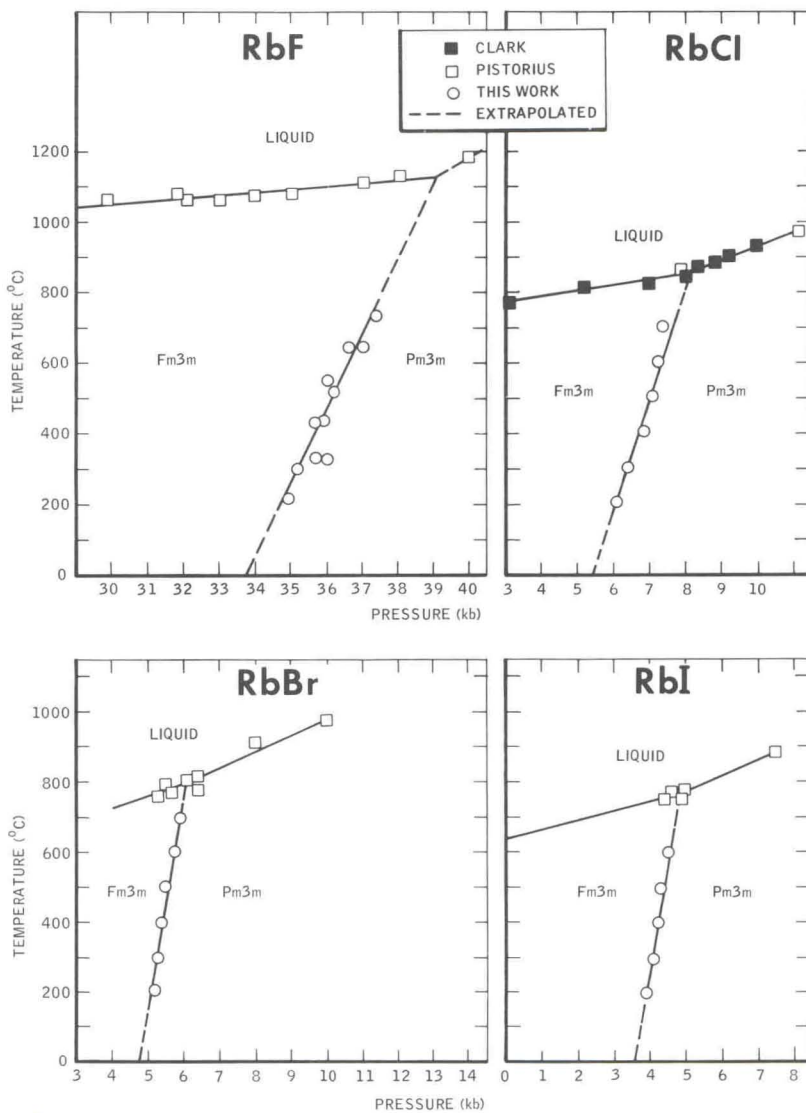


Fig. 2.  $P$ - $V$  diagram for the rubidium halides: □—melting point data of Clark (1959), ■—melting point data of Pistorius (1965, 1966), ○— $Fm\bar{3}m \rightleftharpoons Pm\bar{3}m$  transition, this work.

served in KF at pressures up to 45 kb and at temperatures up to 800°C.

As in the case of most solid-solid phase transitions [21] these salts also show a hysteresis effect. The width of the hysteresis loop is, in general, less than one kilobar at temperatures greater than 200°C, and becomes larger and less reproducible at temperatures below 200°C. We have assumed that the equilibrium

transition pressure is the average of the transition pressures obtained on compression and decompression. In all cases, the equilibrium transition pressure appears, within the experimental accuracy of these data, to be a linear function of the temperature over the interval 200–700°C. These  $P_{tr}$  data were treated by method of least squares to obtain the transition pressure as a function of temperature in

the form

$$P_{tr}(kb) = a + bt \quad (1)$$

where  $P_{tr}$  is the  $Fm3m \rightleftharpoons Pm3m$  transition pressure at a given temperature  $t$  ( $^{\circ}C$ ). Data for the constants  $a$  and  $b$  are given in Table 1. The constant  $b$  is of particular significance since  $b = dP/dT$ . The values for the transition pressure at  $25^{\circ}C$  reported in Table 2 were obtained from extrapolation of the high temperature data, by the use of equation (1).

The transition volumes\* ( $\Delta V_{tr}$ ,  $Fm3m \rightarrow Pm3m$ ) for KCl, KBr and KI at temperatures between  $200$ – $800^{\circ}C$  are shown in Fig. 3. Similarly,  $\Delta V_{tr}$  for RbF, RbCl, RbBr and RbI are shown in Fig. 4. The volume change ( $\Delta V_{tr}$ ) appears to be a linear function of temperature at temperatures above  $200^{\circ}C$ . These data were also treated by method of least squares to obtain the transition volume as a function of temperature in the form

$$\Delta V_{tr}(cm^3/mole) = c + dt \quad (2)$$

where  $\Delta V_{tr}$  is the transition volume at a given temperature  $t$  ( $^{\circ}C$ ). Values for the constants  $c$  and  $d$  are given in Table 1. The transition volumes at  $25^{\circ}C$  reported in Table 3 were obtained from an extrapolation of the high tem-

\*The transition volume vs. temperature data shown in Figs. 3 and 4 are not at constant pressure (except in the special case of KCl where  $dT/dP \approx 0$ ) but are at pressures corresponding to the temperatures along the  $Fm3m \rightleftharpoons Pm3m$  phase boundary.

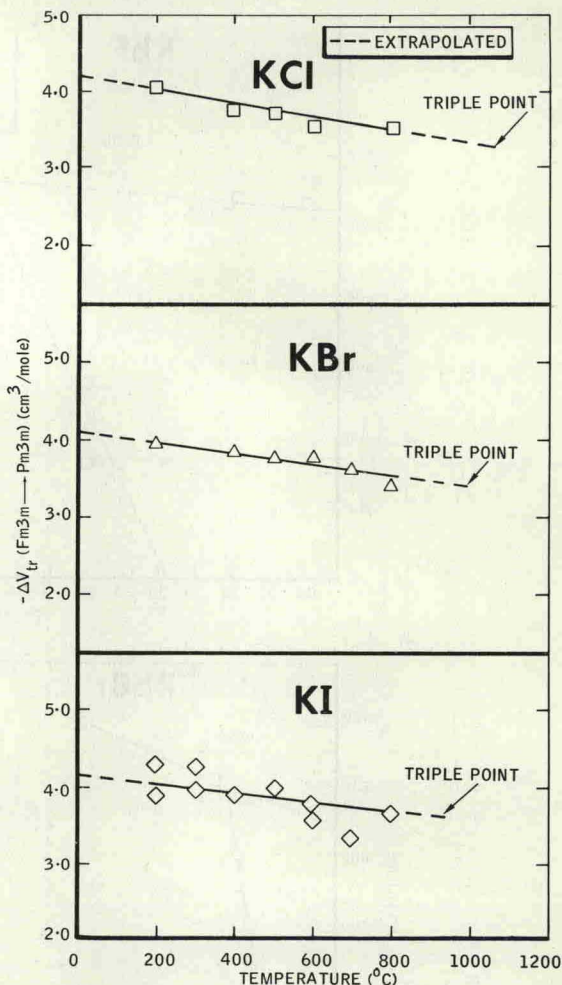


Fig. 3.  $\Delta V(Fm3m \rightarrow Pm3m)$  vs.  $T$  for KCl, KBr and KI.

Table 1. Constants for the temperature dependence of the  $Fm3m \rightleftharpoons Pm3m$  transition pressure [ $P_{tr}(kb) = a + bt$ ] and the transition volume  $Fm3m \rightarrow Pm3m$  [ $\Delta V_{tr}(cm^3/mole) = c + dt$ ] in the potassium and rubidium halides

Salt	$a$ (kb)	$b \times 10^3$ (kb/deg)	$c$ ( $cm^3/mole$ )	$d \times 10^3$ ( $cm^3/mole/deg$ )
KCl	$19.55 \pm 0.13$	$-0.015 \pm 0.256$	$-4.13 \pm 0.01$	$0.830 \pm 0.176$
KBr	$18.02 \pm 0.28$	$-1.186 \pm 0.485$	$-4.19 \pm 0.11$	$0.869 \pm 0.201$
KI	$18.35 \pm 0.20$	$-3.223 \pm 0.387$	$-4.44 \pm 0.15$	$1.211 \pm 0.295$
RbF	$34.37 \pm 0.38$	$+3.723 \pm 0.710$	$-1.84 \pm 0.29$	$0.445 \pm 0.513$
RbCl	$5.61 \pm 0.14$	$+2.800 \pm 0.296$	$-6.96 \pm 0.11$	$2.880 \pm 0.269$
RbBr	$4.88 \pm 0.06$	$+1.371 \pm 0.124$	$-7.47 \pm 0.18$	$1.597 \pm 0.366$
RbI	$3.64 \pm 0.05$	$+1.400 \pm 0.115$	$-8.15 \pm 0.10$	$1.920 \pm 0.236$

Table 2. Transition pressure ( $P_{tr}$ , kb) for the Fm3m ⇌ Pm3m phase change in the potassium and rubidium halides at 25°C

Salt	Bridgman 1945[25]	Daniels, <i>et al.</i> 1966[31]	Kennedy and LaMori, 1962[18]	Knof and Maisch, 1963[26]	Larson, 1965[29]	Piermarini and Weir, 1962[4]	Pistorius, 1964[11, 12]	Pistorius and Snyman, 1964[13]	This work	Average Value
KF						35		14.6 ± 1.3	None observed	
KCl	19.7		18.28 ± 0.21		20.0		19.27 ± 0.08		19.55 ± 0.13	19.4 ± 0.3
KBr	18.0		17.88 ± 0.06		18.5		17.43 ± 0.07		17.99 ± 0.28	18.0 ± 0.2
KI	17.8		17.48 ± 0.24				17.34 ± 0.05		18.27 ± 0.19	17.7 ± 0.3
RbF				33		12		6.1	34.47 ± 0.38	33.8 ± 0.8
RbCl	4.90						5.28		5.68 ± 0.14	5.32 ± 0.24
RbBr	4.50						4.20 ± 0.2		4.92 ± 0.06	4.57 ± 0.35
RbI	3.96	3.54					3.59 ± 0.16		3.68 ± 0.05	3.69 ± 0.11

Table 3. Transition volume ( $-\Delta V_{tr}$ , cm<sup>3</sup>/mole) for the Fm3m → Pm3m phase change in the potassium and rubidium halides at 25°C

Salt	Adams and Davis, 1962[8]	Bridgman, 1945[25]	Genshaft <i>et al.</i> , 1967[30]	Jacobs, 1938[6]	Jamison, 1957[7]	Nagasaki and Minomura, 1964[9]	Pistorius and Snyman, 1964[13]	Weir and Piermarini, 1964[5]	This work	Average value
KF							1.0	2.49	None Obs.	
KCl		4.20				3.85		6.85	4.11 ± 0.10	4.05 ± 0.17
KBr		4.55						8.35	4.17 ± 0.11	4.36 ± 0.19
KI		4.50			4.50			11.8	4.41 ± 0.15	4.47 ± 0.13
RbF								3.70	1.83 ± 0.29	
RbCl	6.55	6.00	6.30					5.76	6.95 ± 0.11	6.30 ± 0.35
RbBr		6.55						6.60	7.43 ± 0.18	6.86 ± 0.39
RbI	9.65	7.50		7.9				8.26	8.10 ± 0.10	8.28 ± 0.31

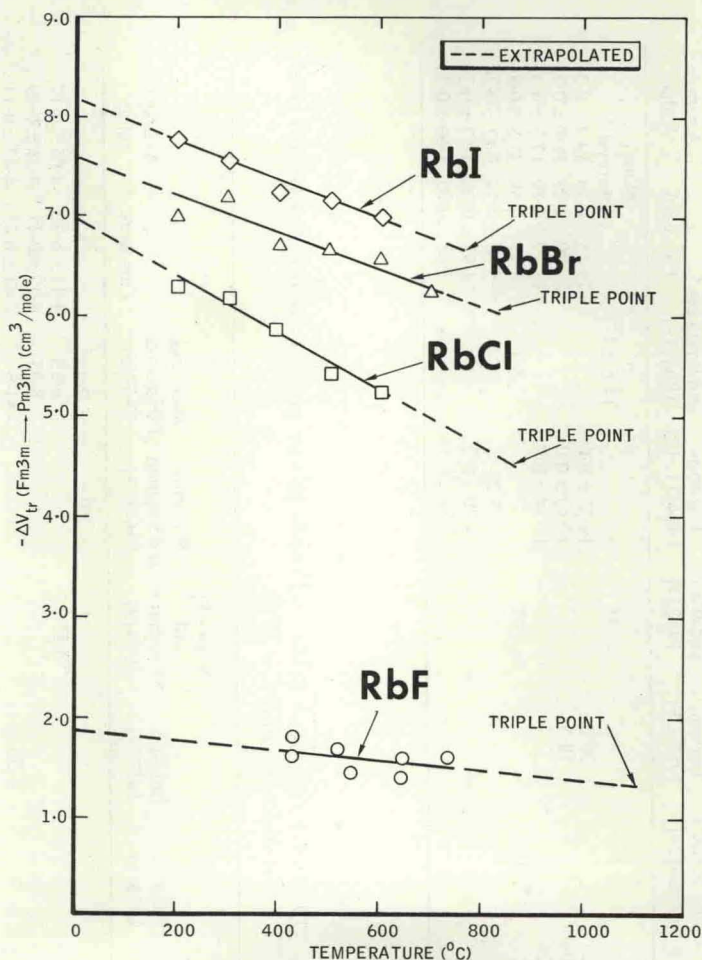


Fig. 4.  $\Delta V(\text{Fm3m} \rightarrow \text{Pm3m})$  vs.  $T$  for the rubidium halides.

perature data by use of equation (2). The pressure-temperature coordinates of the  $\text{Fm3m} \rightleftharpoons \text{liquid} \rightleftharpoons \text{Pm3m}$  triple point for these salts were determined from the intersection of the melting curves of the  $\text{Fm3m}$  and  $\text{Pm3m}$  phases at the  $\text{Fm3m} \rightleftharpoons \text{Pm3m}$  phase boundary. The melting curves of the  $\text{Fm3m}$  and  $\text{Pm3m}$  phases were drawn through the data points of Clark[22] and of Pistorius [23] in order that the intersection of these two curves would fall on the  $\text{Fm3m} \rightleftharpoons \text{Pm3m}$  phase boundary obtained in this work. Triple point coordinates obtained for the salts  $\text{KCl}$ ,  $\text{KBr}$  and  $\text{KI}$  are shown in Fig. 1; coordinates for the rubidium halides are shown in Fig. 2.

These triple point P-T coordinates are compared with the P-T coordinates given by Clark[22] and by Pistorius[23] in Table 4.

#### Potassium halides

Potassium fluoride was examined at pressures up to 45 kb at approx. 100° intervals from room temperature up to 800°C. However, we fail to find the phase transition reported by Weir and Piermarini[5] and by Pistorius and Snyman[13]. Pistorius *et al.* found the volume change of this transition to be small, i.e. 0.5 per cent. The sensitivity of the method used here is more than adequate to detect a phase transition with such a small

Table 4. Thermodynamic properties of the Fm3m → Pm3m transition in the potassium and rubidium halides at the Fm3m ⇌ liquid ⇌ Pm3m triple point

Salt	Clark[22]		Pistorius[23]		This work						
	<i>P</i> (kb)	<i>T</i> (°C)	<i>P</i> (kb)	<i>T</i> (°C)	<i>P</i> (kb)	<i>T</i> (°C)	$-\Delta V_{tr}$ (cm <sup>3</sup> /mole)	$\Delta S_{tr}$ (cal/mole/deg)	$T_{\Delta S}$ (cal/mole)	<i>P</i> (cal/mole)	$\Delta E$ (cal/mole)
KF					none observed						
KCl	18.95 ± 0.1	1042 ± 5	18.7 ± 0.7	1050 ± 10	19.5 ± 0.3	1070 ± 10	3.24 ± 0.21	+ 0.001	17	- 1520	- 1540
KBr			16.8 ± 1.0	997 ± 10	16.8 ± 0.6	1005 ± 10	3.32 ± 0.18	+ 0.09	120	- 1340	- 1460
KI			16.9 ± 1.5	934 ± 15	15.3 ± 0.4	940 ± 15	3.31 ± 0.19	+ 0.25	308	- 1210	- 1520
RbF			32	1055	38.5 ± 0.8	1105 ± 15	1.39 ± 0.55	- 0.12	- 170	- 1280	- 1110
RbCl	7.80	852	7.80 ± 0.01	852 ± 5	8.1 ± 0.3	870 ± 5	4.45 ± 0.18	- 0.30	- 344	- 860	- 520
RbBr			6.1 ± 0.8	808 ± 10	6.0 ± 0.2	830 ± 10	6.15 ± 0.23	- 0.20	- 222	- 880	- 660
RbI			5.0 ± 0.8	760 ± 10	4.7 ± 0.2	763 ± 10	6.69 ± 0.16	- 0.22	- 233	- 750	- 520

volume change. Since we find no polymorphic change at high temperatures where the transition kinetics would be more favorable, and the fact that Pistorius[23] found no break in the melting curve suggests that KF has no solid-solid transition at pressures below 45 kb.

The  $Fm3m \rightleftharpoons Pm3m$  transition pressures found for the salts KCl, KBr and KI are compared in Table 2 with the transition pressures reported in the literature. Bridgman has examined this transition in these salts on three separate occasions[3, 24, 25]; however, only the latest of Bridgman's data[25] are given. In general our results for  $P_{tr}$  are in good agreement with the published data (Table 2). Average values of  $P_{tr}$  were in each case calculated from the data tabulated in Table 2.

Bridgman[3] and Pistorius[11, 12] have examined the effect of temperature on the transition pressure in these salts over the temperature range 25°–200°C. Bridgman[3] gives +3.45, –4.54 and +3.33 bar/deg respectively for the temperature dependence of the transition pressure in KCl, KBr and KI. Pistorius [11, 12], on the other hand, gives –0.25, +0.55 and –1.88 bar/deg for these same salts. These data are compared with the constant  $b$  from Table 1, i.e. the value of  $dP/dT$  found in this work. The data from these three sources all indicate that the variation of  $P_{tr}$  with temperature is small. It is seen that the values of  $dP/dT$  found by Bridgman and Pistorius all disagree in sign. The sign of  $dP/dT$  however determines the sign of the entropy change,  $\Delta S_{tr}$  ( $Fm3m \rightarrow Pm3m$ ) for this transition in these salts since  $\Delta V_{tr}$  ( $Fm3m \rightarrow Pm3m$ ) is negative in all cases.

The agreement between  $\Delta V_{tr}$  for KCl, KBr and KI found here and with published data (Table 3) is also relatively good, with the exception of the  $\Delta V_{tr}$  data given by Weir and Piermarini[5]. Weir *et al.* obtained their transition volume data from high pressure X-ray diffraction studies. Their data, however, are also in disagreement with the  $\Delta V_{tr}$  data given by Jamieson[7] and by Nagasaki *et al.*[9] for KI and KCl respectively. (The latter data for

KI and KCl were also determined from X-ray diffraction studies carried out at high pressures.) These  $\Delta V_{tr}$  data of Weir *et al.*[5] were not used in the calculation of the average value of  $\Delta V_{tr}$  for the salts KCl, KBr and KI.

#### *Rubidium halides*

Piermarini and Weir[4] report a solid-solid phase transition in RbF at a pressure between 9 and 15 kb. They give the volume change for this transition as –20 per cent. Knof and Maisch[26] have observed changes in the optical transmission properties of RbF at a pressure of 33 kb, which is similar to the optical effect associated with the  $Fm3m \rightarrow Pm3m$  transition in the potassium halides, KCl and KBr. Pistorius and Snyman[13], on the other hand, report phase transitions in RbF at a pressure of 6.1 kb at a temperature of 20°, and 5.0 kb at 200°C. The latter authors[13] noted that this phase transition in RbF was very sluggish. No indication of the size of  $\Delta V$  for this transition was given by Pistorius *et al.*[13].

The results from our dilatometric measurements clearly indicate a polymorphic transition in RbF at about 35 kb, in agreement with the results reported by Knof *et al.*[26]. Transition pressure data for RbF are shown in Fig. 2. The transition was very sluggish at 100° and no transition was observed at room temperatures. However, at temperatures above 300°C the transition proceeds as readily as was found in the other alkali halides at 200°C. In the case of RbF, data taken only above 300°C were used in the least squares treatment of  $P_{tr}$  and  $\Delta V_{tr}$  vs. temperature. It was also necessary to modify the experimental arrangement since at temperatures above 400°C RbF reacts with the graphite heater causing it to become relatively non-conducting. Pistorius[23] found Ni to be a satisfactory container for RbF at high temperatures. We therefore isolated our sample from the graphite heater with a thin (0.0025 cm) nickel sleeve. With this modification our measurements were still limited to temperatures below about



750°C since an irreversible change occurs in the resistance of graphite at higher temperatures, presumably from attack by RbF through the nickel foil. Our RbF samples were examined by X-ray diffraction after being removed from the pressure chamber and showed diffraction lines characteristic of only the Fm3m phase. Data for  $P_{tr}$  and  $\Delta V_{tr}$  for this salt at 25°C are given in Tables 2 and 3 respectively.

The pressures obtained for the Fm3m  $\rightleftharpoons$  Pm3m transition in the rubidium halides are compared with the published values in Table 2. Averages of  $P_{tr}$  for each of these salts were calculated from data given in Table 2. However, in the case of RbF only the data of Knof and Maisch[26] were averaged with the data from this work. Pistorius[11, 12] gives the temperature dependence of the polymorphic transition pressure in RbCl, RbBr and RbI as 3.01, 2.19 and 1.94 bar/deg respectively. The agreement with  $dP/dT$  found here ( $b$  in Table 1) is better than in the case of the potassium salts.

#### Thermodynamic calculations

The average values of  $P_{tr}$  and  $\Delta V_{tr}$  given in Tables 2 and 3 were used to calculate the thermodynamic properties of this polymorphic transition in these salts at a temperature of 298°K. However in the case of  $dP/dT$ , we

have used only the values obtained in this work, since our measurements are over a much wider temperature interval (from 400°C to as much as 700°C) than were Bridgman's [24] and Pistorius'[12, 13] work.

At a temperature and pressure where the two polymorphs may be considered to be in equilibrium, then

$$G(\text{Fm3m phase}) = G(\text{Pm3m phase}). \quad (3)$$

Thus

$$\Delta G = 0 \quad (4)$$

and at constant temperature and pressure

$$\Delta E = P\Delta V - T\Delta S. \quad (5)$$

The external  $P\Delta V$  work necessary to carry out the Fm3m  $\rightarrow$  Pm3m phase transformation (reversibly) at constant pressure and temperature is calculated from the average values of  $P_{tr}$  and  $\Delta V_{tr}$ . These data for  $P\Delta V$  at 298°K are given in Table 5. Data for  $P\Delta V$  reported by Weir *et al.*[5] are also shown. The larger values of  $P\Delta V$  reported by these authors[5] for the potassium salts arise from the larger transition volumes found by them. On the other hand, good agreement in case of RbF is fortuitous since Weir's much lower value of  $P_{tr}$  is compensated for by the larger value of

Table 5. Thermodynamic properties of the Fm3m  $\rightarrow$  Pm3m transition in the potassium and rubidium halides at 298°K

Salt	$\Delta S_{tr}$	$\Delta S_{tr}^*$	$T\Delta S$	$P\Delta V$	$P\Delta V^\dagger$	$\Delta E$
	Pistorius[11, 12] (cal/mole/deg)	This work (cal/mole/deg)	This work (cal/mole)	Weir <i>et al.</i> [5] (cal/mole)	This work (cal/mole)	This work (cal/mole)
KCl	+0.03	0.002	6	-3.000	-1880	-1890
KBr	-0.11	0.12	37	-3.300	-1880	-1920
KI	+0.53	0.34	103	-4.500	-1890	-1990
RbF		-0.16	-48	-1.300	-1490	-1440
RbCl	-0.44	-0.42	-125	-700	-800	-675
RbBr	-0.35	-0.23	-67	-700	-750	-680
RbI	-0.38	-0.28	-83	-700	-730	-660

\* Average values of  $\Delta V_{tr}$  in Table 4 were used to calculate these entropies.

† Average value of  $P_{tr}$  in Table 1 and average value of  $\Delta V_{tr}$  in Table 4 were used to calculate this  $P\Delta V$  product.

$\Delta V$ . The agreement of  $P\Delta V$  from this work and from Weir's is, however, relatively good in the case of RbCl, RbBr and RbI.

The entropy change ( $\Delta S_{tr}$ , Fm3m  $\rightarrow$  Pm3m) was calculated from the Clausius Clapeyron relation. Data obtained for  $\Delta S_{tr}$  at 298°K are given in Table 5. Similarly, Pistorius[12, 13] has calculated  $\Delta H$  for this polymorphic transition in these salts from his value of  $dP/dT$  and from Weir's and Piermarini's [5] transition volume. As noted above, Weir's value of  $\Delta V_{tr}$  for the potassium salts are considerably higher than the results found by others (results, on the other hand, for the rubidium salts RbCl, RbBr and RbI are in good agreement, Table 2). The entropy of transformation derived from Pistorius' calculations are  $-0.44$ ,  $-0.35$  and  $-0.38$  cal/mole/deg respectively for RbCl, RbBr and RbI. The agreement between the  $\Delta S_{tr}$  calculated by Pistorius[12, 13] and those derived from this work is relatively good for these salts.

Data for the  $T\Delta S$  term in equation (5) are given in Table 5 as also the data for the change in internal energy ( $\Delta E$ ) associated with this polymorphic transformation. Similarly, thermodynamic properties for this Fm3m  $\rightarrow$  Pm3m transformation at the triple point are given in Table 4.

Several trends in the transition properties of these salts are noted. From Figs. 4 and 5, it is seen that in all cases studied, the absolute value of transition volume decreases with an increase in temperature. In general, the pressure of the Fm3m  $\rightleftharpoons$  Pm3m transition is relatively insensitive to temperature for the halides of these two alkali metals. The potassium salts do, however, show a small decrease whereas the rubidium salts show a correspondingly small increase in transition pressure with an increase in temperature. The transition pressure for CsCl is also known to increase with an increase in temperature[27]. Consequently, at constant pressure  $\Delta S$  (Fm3m  $\rightarrow$  Pm3m) is positive for the potassium halides and negative for the rubidium halides (and CsCl). Thus in the case of the alkali

chlorides, the absolute entropy of the Fm3m phase becomes larger relative to the Pm3m phase as the cation increases in atomic number and therefore in size. A similar trend has been noted[28] in the fusion of the Fm3m phase of these chlorides.

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