

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