

Salt	Clark[22]	Pistorius[23]	This work
KF	18.95 ± 0.1	1042 ± 5	
KCl	18.7 ± 0.7	1050 ± 10	19.5 ± 0.3
KBr	16.8 ± 1.0	997 ± 10	16.8 ± 0.6
KI	16.9 ± 1.5	934 ± 15	15.3 ± 0.4
RbF	32	1055	38.5 ± 0.8
RbCl	7.80 ± 0.01	852 ± 5	8.1 ± 0.3
RbBr	6.1 ± 0.8	808 ± 10	6.0 ± 0.2
RbI	5.0 ± 0.8	760 ± 10	4.7 ± 0.2
			none observed
			1070 ± 10
			1005 ± 10
			940 ± 15
			3.31 ± 0.19
			$+0.25$
			308
			120
			$+0.09$
			3.24 ± 0.21
			$+0.001$
			17
			-1520
			-1460
			-1520
			-1110
			-860
			-880
			-750
			-520

Table 4. Thermodynamic properties of the $Fm\bar{3}m \rightarrow Pm\bar{3}m$ transition in the potassium and rubidium halides at the $Fm\bar{3}m \rightleftharpoons liquid \rightleftharpoons Pm\bar{3}m$ triple point

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, ΔS_{tr} ($Fm3m \rightarrow Pm3m$) for this transition in these salts since ΔV_{tr} ($Fm3m \rightarrow Pm3m$) is negative in all cases.

The agreement between ΔV_{tr} for KCl, KBr and KI found here and with published data (Table 3) is also relatively good, with the exception of the ΔV_{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 ΔV_{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 ΔV_{tr} data of Weir *et al.*[5] were not used in the calculation of the average value of ΔV_{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 ΔV 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 ΔV_{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