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						
	P (kb)	T (°C)	P (kb)	T (°C)	P (kb)	T (°C)	$-\Delta V_{tr}$ (cm³/mole)	ΔS_{tr} (cal/mole/deg)	$T_{\Delta}S$ (cal/mole)	P (cal/mole)	ΔE (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 ⇄ 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 → Pm3m) for this transition in these salts since ΔV_{tr} (Fm3m → 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 transaction 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 → 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