THERMODYNAMICS OF THE Fm3m ⇌ Pm3m TRANSITION IN THE POTASSIUM AND RUBIDIUM HALIDES*

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Abstract—The Fm3m ⇌ 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 (ΔV_{tr}) measured for these polymorphic transitions were treated by method of least squares. Averages of P_{tr} and ΔV_{tr} at 25° were taken from this work and from data in the literature. These average values of P_{tr} and ΔV_{tr} were used to calculate the $P\Delta V$ work for this transition; the entropy change (ΔS_{tr}) was calculated from the average value of ΔV_{tr} and the temperature coefficient, (dP_{tr}/dT). Data are also given for P_{tr}, ΔV_{tr} and ΔS_{tr} at the triple point (Fm3m ⇌ liquid ⇌ 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 ΔS (Fm3m → Pm3m) is positive for the potassium salts KCl, KBr and KI; for the rubidium halides it is negative. The transition volume ΔV(Fm3m → 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 ∼ 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 ~ 200°C, imposed by external heating of the compound cylinder apparatus, to temperatures of ~ 1000°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 ΔV_{tr} measure-

ments at higher temperatures, i.e. $t > 200°C$, 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 Bi(I) ⇌ Bi(II) and Bi(II) ⇌ Bi(III) at 25°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°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° intervals, from 25 to 700°C and in some cases up to 800°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-
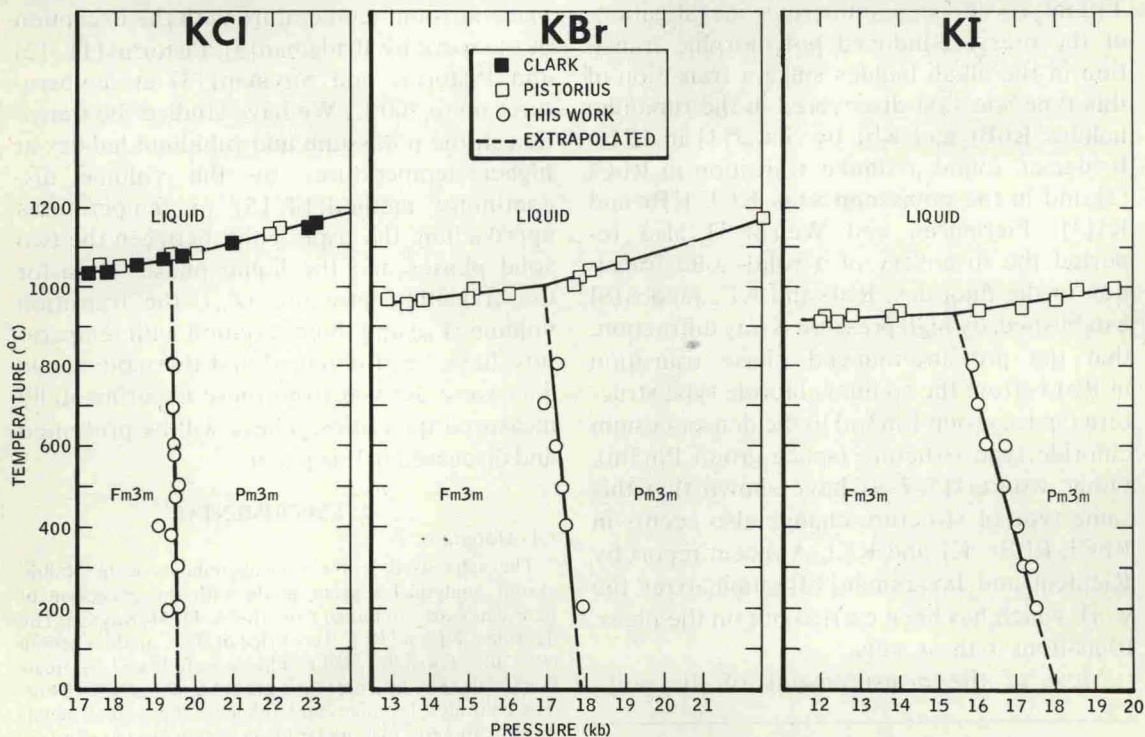

Fig. 1. *PV* diagram for the potassium halides KCl, KBr and KI: ■ — melting point data of Clark (1959), □ — melting point data of Pistorius (1965, 1966), ○ — Fm3m ⇌ Pm3m transition, this work.