

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 ΔV_{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 ΔV_{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 ΔV_{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 | ΔS_{tr} | ΔS_{tr}^* | $T\Delta S$ | $P\Delta V$ | $P\Delta V^\dagger$ | ΔE |
|------|-------------------------------------|-----------------------------|-------------------------|--------------------------------------|-------------------------|-------------------------|
| | 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 ΔV_{tr} in Table 4 were used to calculate these entropies.

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

ΔV . 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 (ΔS_{tr} , Fm3m \rightarrow Pm3m) was calculated from the Clausius Clapeyron relation. Data obtained for ΔS_{tr} at 298°K are given in Table 5. Similarly, Pistorius[12, 13] has calculated ΔH 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 ΔV_{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 ΔS_{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 (ΔE) 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 ΔS (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.

Acknowledgements—The authors are indebted to Dr. S. J. Yosim for his continued interest and many helpful discussions during the course of this work, and to Dr. Maynard Hiller for preparing the samples of KF and RbF.

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