Polymorphism in KCl–RbCl and KCl–KBr Solid Solutions at High Pressure*

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The pressure-induced polymorphic transition in solid solutions of KCl–RbCl and KCl–KBr systems was investigated by dilatometry over the temperature interval 25–800°C. This transition is similar to the $Fm3m \rightleftarrows Pm3m$ phase change which occurs in the component salts at high pressure. However, the transition is broader, i.e., occurs over a larger pressure interval, than was found in the pure component salts. Data for the mean transition pressure (P_{tr}^m) and total volume change (ΔV_{tr}) for this transition in these solid solutions are given for the temperature range 200–800°C. As an approximation, P_{tr}^m has been treated in the same manner as the transition pressure for a pure salt to calculate $P\Delta V$, ΔS, and ΔE for the polymorphic transition in these solid solutions. These properties change in a continuous, but nonlinear, manner upon substitution of RbCl and KBr into the KCl structure. Both cationic substitution (Rb^+ for K^+) and anionic substitution (Br^- for Cl^-) increase the interatomic spacing by approximately the same amount. However, cationic substitution (the smaller ions) has a greater effect on the transition properties than does anionic substitution.

I. INTRODUCTION

It is well-known that the alkali halides occur in two crystalline forms. The halides of cesium normally have the CsCl-type structure, space group $Pm3m$ (CsF excepted). Halides of lithium, the smallest of the alkali metals, have been observed only in the "rock salt" form, space group $Fm3m$. Halides of the alkali metals of intermediate size (Na, K, and Rb) normally have the $Fm3m$ structure, but in many cases these salts transform to the $Pm3m$ form at elevated pressure (*1–4*).[1] The normal occurrence of the phases in this class of compounds is, in general, in accordance with the relative stability of these structure types as is predicted from radius ratio considerations (*10, 11*).

Trends associated with atomic number or size of the ions are known to exist in some of the thermodynamic properties of this $Fm3m \rightleftarrows Pm3m$ transition. For example, some of the cesium salts undergo this polymorphic transition when heated at atmospheric pressure. The rubidium salts undergo this change at ordinary temperatures but at pressures of 4–6 kb, the potassium salts likewise at pressures from

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[1] The literature on the phase transition in this class of compounds is extensive. For further information the reader is referred to papers by Tosi and Fumi (*5*), Schumacher (*6*), Tosi (*7*), Klement and Jayaraman (*8*), and Darnell and McCollum (*9*).

18–20 kb, while the rock salt form of NaCl transforms to the CsCl structure at a pressure of 300 kb (12). In a recent paper Darnell and McCollum (9) have found other trends in this polymorphic transition in this group of salts, e.g., the transition volume of the rubidium chloride, bromide, or iodide is greater than for the corresponding potassium salt. Furthermore, the entropy change, $\Delta S(Fm3m \to Pm3m)$, is positive for the potassium salts but negative for the rubidium salts (and CsCl). Indeed such trends in this polymorphic transition should not be surprising since similar trends in the temperature, volume, and entropy of the melting of the $Fm3m$ phase of these salts (i.e., $Fm3m \to$ liquid) are known (13).

In order to gain more insight into the polymorphic transition in this class of compounds we have therefore examined this phase transition in the very nearly ideal solid solutions of the KCl–RbCl (cation substitution) (14) and KCl–KBr (anion substitution) (15) systems. This is analogous in some respects to the work of Menary, Ubbelohde, and Woodward (16), Wood and co-workers (17–19), Krogh-Moe (20, 21), and Rao et al. (22) on the effect of ionic substitution upon the thermally induced (atmospheric pressure) $Pm3m \rightleftarrows Fm3m$ transition in CsCl.

II. EXPERIMENTAL

A. Materials

The salts KCl, KBr, and RbCl used in these measurements were Mallinckrodt analytical reagent grade. These salts were out-gassed for a period of 24 hr under high vacuum ($p < 10^{-6}$ Torr) at 150°C. The component salts for a given solid solution were weighed, with a precision necessary to yield mole ratios known to within one part in one thousand, and then mixed in a molten state. This molten salt solution was rapidly chilled by pouring it into a thin layer (1 mm) on the bottom of a Pt crucible. The resulting solid solution was then homogenized by keeping it for several hours at a temperature $\sim 100°$ below the temperature of the solidus curve (23). These solid solutions were pulverized and then compressed into pellets 0.6 by 1.5 cm at a pressure of 2 kb. X-ray powder patterns show this technique gives solid solutions with a uniform composition. Lattice parameters (a_0, one atmosphere) were calculated from an average of five separate back reflections.

The results obtained here are in excellent agreement with the lattice parameters reported for the component salts KCl, KBr, and RbCl by Swanson et al. (24, 25), as well as for the solid solutions of KCl–RbCl reported by Havighurst et al. (26), and the KCl–KBr system reported by Oberlies (27). As is well-known in the literature (26, 27) the lattice parameters of these two binary solid solutions varies linearly with mole fraction (x) of the component salts, i.e.,

$$a_0(\text{solid solution}) \cong x_1 a_{0_1} + (1-x_1)a_{0_2}. \tag{1}$$

B. Apparatus and Procedure

The experimental methods used to measure the transition pressure and transition volume of these solid solutions of KCl–RbCl and KCl–KBr were, in general, similar to the methods employed for the component salts (9). The equilibrium transition pressure (P_{tr}) for the component salts KCl, RbCl, and KBr was determined from an average of the pressures at which the phase transition initiates upon compression
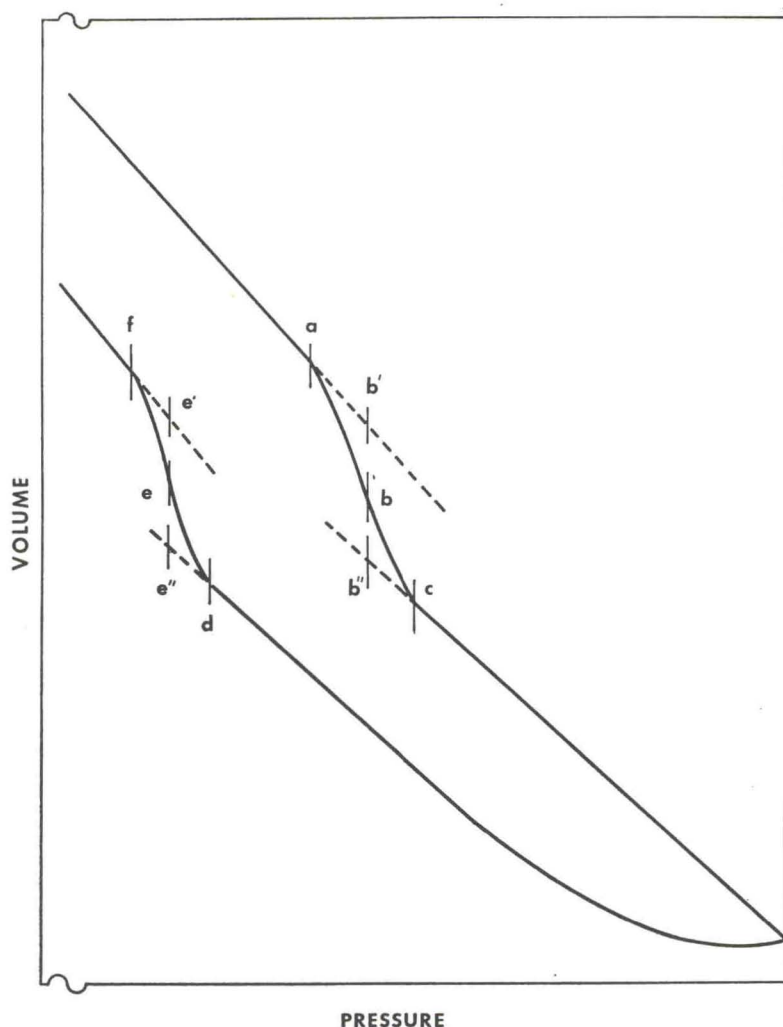
FIG. 1. P–V curve for $K(Cl_{0.5}Br_{0.5})$ at 500°C. Upper curve is for compression; lower curve for decompression.

and decompression, i.e., from Fig. 1,

$$P_{tr} = \frac{P_a + P_d}{2}. \tag{2}$$

This is similar to the technique employed by Jayaraman et al. (28). In the case of the pure salts we find that an average of the midpoint of the transition pressure for the compression and decompression yields essentially the same value for P_{tr}, i.e., with reference to Fig. 1, $(P_a + P_d)/2 \cong (P_b + P_e)/2$. Although the transition in a solid solution at constant temperature from thermodynamic considerations should occur over a finite pressure interval (29, 30), we have considered the midpoint of the

transition pressure interval in these solid solutions as though it were an equilibrium transition pressure of a pure component. With reference to Fig. 1, the midpoint of the transition pressure upon compression, P_b, is $(P_a + P_c)/2$; for decompression it is equal to $(P_d + P_f)/2$. Averaging these midpoints we obtain the mean transition pressure P_{tr}^m, where

$$P_{tr}^m = \frac{P_b + P_e}{2}. \tag{3}$$

The "width" of the transition pressure interval is given by $P_c - P_a$ and $P_d - P_f$ (see Fig. 1) for the compression and decompression processes, respectively. Ideally for the pure salts this width should be equal to zero. In actual practice this is not found to be the case even at temperatures approaching the melting point (9). Hysteresis and pressure gradients within the sample contribute to the width of this pressure interval in the pure salts; in the solid solutions there may also be a broadening since the transition may have finite width. The "width" of this transition (P_w) was determined for both the pure salts and the solid solutions from

$$P_w = \frac{(P_c - P_a) + (P_d - P_f)}{2}, \tag{4}$$

with pressure–volume coordinates defined in Fig. 1.

The volume change associated with this solid–solid phase transition was obtained from extrapolation of the pre- and post-transition segments of the P–V curves (Fig. 1) to the pressures P_b and P_e. These points represent the midpoint of the transition pressure in the compression and decompression processes, respectively. Thus upon compression, $\Delta V_{\text{compression cycle}} = V_{b''} - V_{b'}$; upon decompression, $\Delta V_{\text{decompression cycle}} = V_{e'} - V_{e''}$. The average volume change for the transition (ΔV_{tr}) was determined from

$$\Delta V_{tr} = \pm \frac{[(V_{e'} - V_{e''}) - (V_{b''} - V_{b'})]}{2}, \tag{5}$$

where the positive sign applies to $\Delta V_{tr}(Pm3m \rightarrow Fm3m)$ and the negative sign to the reverse reaction.

III. RESULTS AND DISCUSSION

The mean pressure (P_{tr}^m) at which solid solutions of salts in the KCl–RbCl and KCl–KBr systems undergo a polymorphic transition was determined at approximately 100° intervals from room temperature to 700°C (800°C in some cases). The results for the salts $(K_{0.75}Rb_{0.25})Cl$, $(K_{0.50}Rb_{0.50})Cl$, $(K_{0.25}Rb_{0.75})Cl$, $K(Cl_{0.75}Br_{0.25})$, $K(Cl_{0.50}Br_{0.50})$, and $K(Cl_{0.25}Br_{0.75})$ are shown in Fig. 2. For comparison, the transition pressures (P_{tr}) for the pure salts KCl, RbCl, and KBr (9) are also shown in Fig. 2. The mean transition pressure (P_{tr}^m) for these solid solutions, as was found in the case for the pure salts (9), is a linear function of the temperature over the interval 200°C to 800°C. The least-squares fit of these data for each of these solid solutions is given in the form

$$P_{tr}^m(kb) = a + bt \ (°C), \tag{6}$$

where P_{tr}^m is the midpoint of the polymorphic transition as defined by Eq. (3); a and b are constants. The coefficient b is of particular interest since it gives the temperature
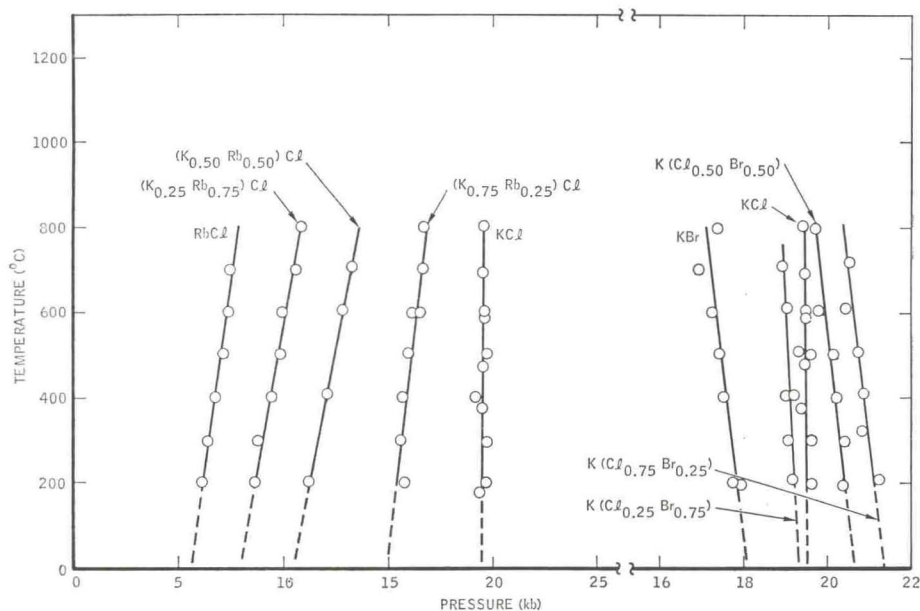
FIG. 2. Transition pressure (P_{tr}^m) vs temperature for the polymorphic phase change in the systems KCl–RbCl and KCl–KBr.

variation of the mean transition temperature, i.e., $b = dP_{tr}^m/dT$. Values of a and b for these solid solutions and for the component salts (9) are given in Table 1. In each case this transition pressure vs temperature equation has been extrapolated (dashed line in Fig. 2) to obtain the transition pressure at 25°C. In this experimental technique we think the values of the transition pressures obtained at 25°C by this extrapolation are more reliable than our directly determined values of P_{tr}^m at 25°C.

TABLE 1

CONSTANTS FOR THE TEMPERATURE DEPENDENCE OF THE POLYMORPHIC TRANSITION
PRESSURE $[P_{tr}^m(kb) = a + bt\,(°C)]$ AND THE POLYMORPHIC TRANSITION VOLUME
$[V_{tr}(cm^3/mole) = c + dt\,(°C)]$ FOR SALTS IN THE SYSTEMS KCl–RbCl AND KCl–KBr

Salt	a (kb)	$b \times 10^3$ (kb/deg)	c (cm³/mole)	$d \times 10^3$ (cm³/mole/deg)
KCl[a]	19.55 ± 0.13	-0.02 ± 0.26	-4.13 ± 0.01	0.83 ± 0.18
$(K_{0.75}Rb_{0.25})Cl$	15.15 ± 0.19	$+1.93 \pm 0.35$	-4.49 ± 0.12	1.04 ± 0.22
$(K_{0.50}Rb_{0.50})Cl$	10.40 ± 0.01	$+4.00 \pm 0.04$	-4.96 ± 0.10	1.55 ± 0.21
$(K_{0.25}Rb_{0.75})Cl$	7.84 ± 0.02	$+3.71 \pm 0.43$	-5.70 ± 0.07	2.10 ± 0.14
RbCl[a]	5.61 ± 0.14	$+2.80 \pm 0.30$	-6.96 ± 0.11	2.88 ± 0.27
$K(Cl_{0.75}Br_{0.25})$	21.23 ± 0.17	-1.37 ± 0.35	-3.90 ± 0.04	0.73 ± 0.09
$K(Cl_{0.50}Br_{0.50})$	20.76 ± 0.14	-1.54 ± 0.29	-3.89 ± 0.08	0.73 ± 0.17
$K(Cl_{0.25}Br_{0.75})$	19.00 ± 0.15	-0.90 ± 0.33	-3.78 ± 0.12	0.47 ± 0.21
KBr[a]	18.02 ± 0.28	-1.19 ± 0.49	-4.19 ± 0.11	0.87 ± 0.20

[a] Darnell and McCollum, Ref. (9).

This is because the much larger frictional and hysteresis effects at 25°C (as compared to $t > 200°C$) lead to a greater uncertainty in P_{tr}^m than arises from this extrapolation of the high temperature data. In the case of KCl, RbCl, and KBr the value of P_{tr} at 25°C from a similar extrapolation (9) was found to be in good agreement with the transition pressure reported by other workers using different experimental techniques.

The volume change (ΔV_{tr}) of the polymorphic transition in these solid solutions was also measured over the temperature interval 25°C to about 800°C (Fig. 3). Here also, as in the case of P_{tr}^m, only the data above 200°C have been used. At lower
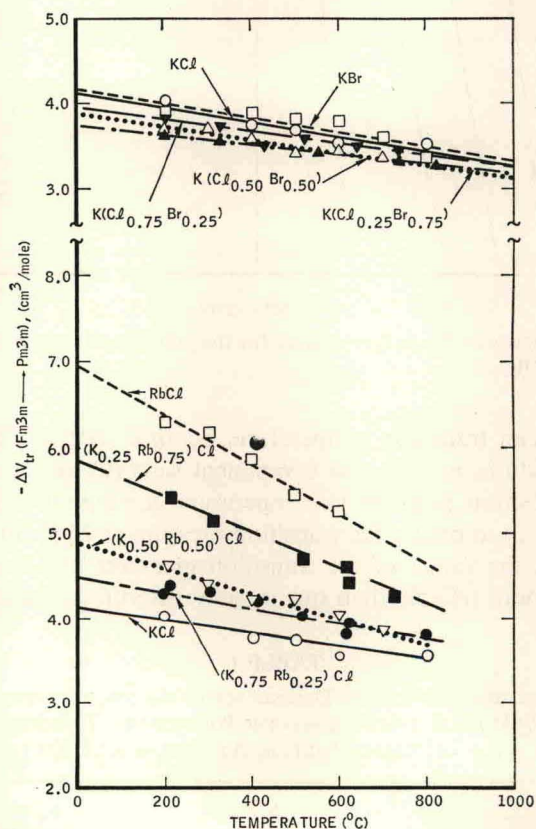

FIG. 3. Volume change of the polymorphic transition for salts in the systems KCl–RbCl and KCl–KBr.

temperatures, where frictional effects, hysteresis, and sluggishness of the transition are more pronounced, it is difficult to obtain a reliable extrapolation of the pre- and post-transition curve to the midpoint of the transition. The transition volume at a given temperature $t(°C)$ is represented by

$$\Delta V_{tr} \ (cm^3/mole) = c + dt \ (°C),   \qquad (7)$$

where c and d are constants. Values of c and d obtained by least-squares treatment of the data are given in Table 1. As can be seen from Fig. 3, the difference in specific

volume between these two polymorphs decreases with increasing temperature for the solid solutions and for the pure salts (9).

The $P-V$ curves for these binary solid solutions of the salts KCl–RbCl and KCl–KBr are similar to the $P-V$ curves found for the component salts. A typical pressure–volume curve for these solid solutions is shown in Fig. 1 for the salt $K(Cl_{0.50}Br_{0.50})$ at 500°C. In general, for all compositions examined, we find that the $P-V$ curves for these solid solutions more closely approach the shape of the $P-V$ curves of the pure component salts [and also to the "idealized" curve depicted by Jayaraman et al. (28)] at higher temperatures. This can be seen in Fig. 4, where the average width of
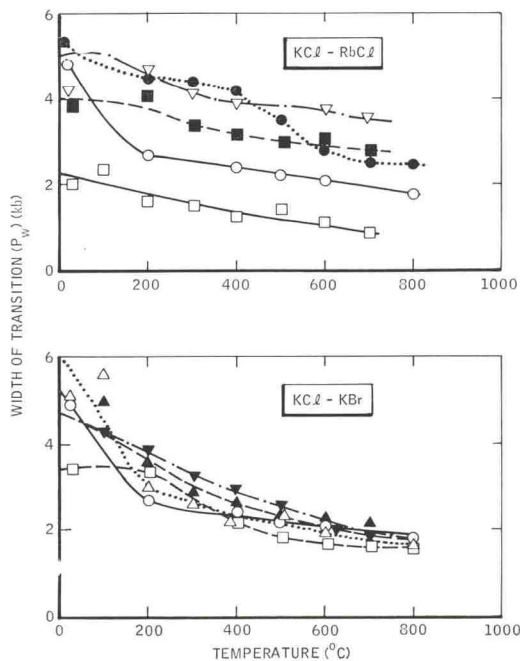

FIG. 4. Width of the polymorphic transition (P_w) vs temperature. In the KCl–RbCl system: KCl $\bigcirc$—$\bigcirc$, $(K_{0.75}Rb_{0.25})Cl$ $\triangledown$—.—$\triangledown$, $(K_{0.50}Rb_{0.50})Cl$ $\blacksquare$ — — $\blacksquare$, $(K_{0.25}Rb_{0.75})Cl$ $\bullet$ . . . . $\bullet$, RbCl $\square$—$\square$. In the KCl–KBr system: KCl $\bigcirc$—$\bigcirc$, $K(Cl_{0.75}Br_{0.25})$ $\blacktriangle$— —$\blacktriangle$, $K(Cl_{0.50}Br_{0.50})$ $\triangle$ . . . . $\triangle$, $K(Cl_{0.25}Br_{0.75})$ $\blacktriangledown$ —.—$\blacktriangledown$, KBr $\square$— —$\square$.

the transition (P_w) in these salts is shown as a function of temperature. Indeed, at 700°C the width of the transition of the solid solutions in the KCl–KBr system is almost identical to P_w for the component salts. However, P_w for solid solutions of KCl–RbCl is still considerably greater than for KCl and RbCl, even at 800°C.

Further insight into the polymorphic transition in these solid solutions may be gained from examination of the pressure–composition ($P-x$) diagrams at constant temperature. In Fig. 5 the width of the transition P_w is shown as a function of composition at three temperatures, 200, 500, and 800°C for the system KCl–RbCl. Similarly, Fig. 6 shows the $P-x$ diagram for the KCl–KBr system at a temperature of 500°C.
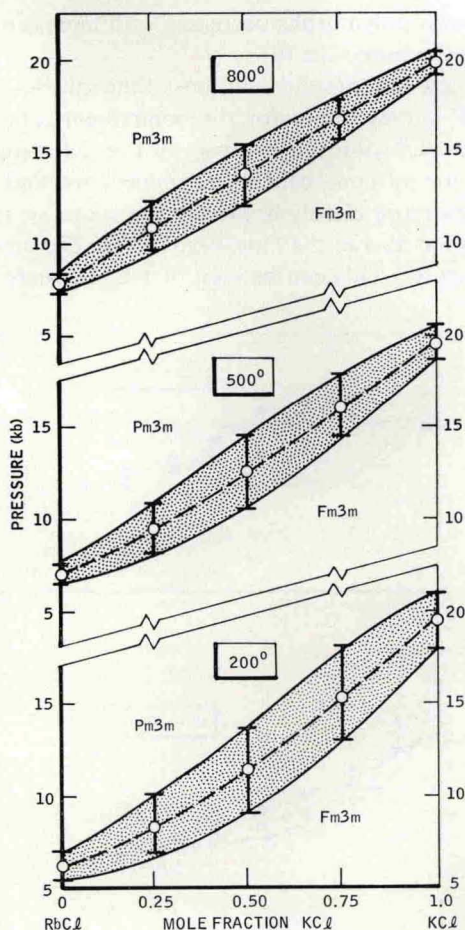
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FIG. 5. Isothermal pressure–composition diagram for the KCl–RbCl system at 200°, 500°, and 800°C.

The larger pressure interval for the polymorphic transition in these solid solutions, in comparison to the interval found for the pure salts, may be due in part to a greater hysteresis effect in the solid solutions. However, it is unlikely that this larger transition pressure interval is due in part to the finite width of the solid–solid transition in this binary system (29, 30). In a P–x diagram such as that illustrated by Figs. 5 and 6 a transition of this type would be outlined by two subsolidus[2] curves, analogous to the solidus–liquidus curves found in the constant pressure T–x diagrams for these systems (23). It is not felt, however, that the subsolidus curves can be obtained by subtraction of the pressure interval due to hysteresis in the case of the pure salts from the pressure interval found in the solid solutions. This is primarily because hysteresis for the solid solutions may be different than for the pure salts. It would

[2] Using the terminology of Ricci (31) phase transitions occurring at temperatures below the liquidus–solidus curves are called "subsolidus."
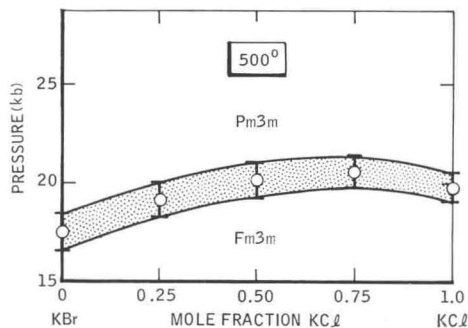
FIG. 6. Isothermal pressure–composition diagram for the KCl–KBr system at 500°C.

appear, however, that upper and lower limits of the subsolidus curves for this transition would be established by the P–x curves in Figs. 5 and 6.

The results from this study suggest that the pressure-induced transition in these solid solutions occurs with a change in structure from the rock salt form to the CsCl form. This would seem reasonable because of the similarity of these pressure-induced phase changes in these solid solutions to the polymorphic transitions found in the component salts (9). The latter are known from high pressure X-ray diffraction studies to undergo the $Fm3m \rightleftarrows Pm3m$ phase change (32, 33). Also by analogy, Wood and co-workers (17, 18) have shown by X-ray diffraction that the temperature-induced (atmospheric pressure) transition in solid solutions of CsCl with RbCl and with CsBr is of the type $Pm3m \rightleftarrows Fm3m$. As mentioned above, the solid solutions of the salts KCl–RbCl and KCl–KBr in their ordinary $Fm3m$ form at atmospheric pressure are approximately ideal in their behaviour.[3] The relatively narrow pressure interval between the upper and lower subsolidus curves in Figs. 5 and 6, particularly at high temperatures, suggests that the high-pressure polymorph is also very nearly an ideal solid solution.

The thermodynamic properties of this polymorphic transition in these solid solutions are calculated, as an approximation, by treating the midpoint of the transition pressure (P_{tr}^m) as if it were an equilibrium transition pressure (P_{tr}) for a pure component. Data given for the transition pressure (P_{tr}^m) and the volume change (ΔV_{tr}) in Columns 2 and 4, respectively, of Table 2 are used to calculate the $P\Delta V$ work necessary to carry out this transition. Similarly the temperature derivative of the mean transition pressure (dP_{tr}^m/dT) given by constant b in Table 1 was used in conjunction with ΔV_{tr} to calculate ΔS_{tr}^m from the Clausius–Clapeyron relation. The values for $P_{tr}^m \Delta V_{tr}$, $T\Delta S_{tr}^m$, and ΔE_{tr}^m for the hypothetical phase transition solid solution (I) → solid solution (II), carried out isothermally at the mean transition pressure P_{tr}^m, are given in Table 2 and are also shown as a function of the mole fraction of KCl in Fig. 7.

Taking KCl as a reference, the effect of ionic substitution upon the properties of this polymorphic transition can now be examined. Formation of solid solutions by

[3] The solid solutions of these salts are considered to be approximately ideal at ambient pressure since their ΔV and ΔH of formation from the pure component salts are not large (34–37).

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TABLE 2

THERMODYNAMIC PROPERTIES OF THE POLYMORPHIC TRANSITION IN THE
KCl–RbCl AND KCl–KBr SYSTEMS AT 298°K

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| Salt	P_{tr}^m (kb)	dT/dP_{tr}^m (°C/kb)	$-\Delta V_{tr}$ (cm^3/mole)	$-P_{tr}^m \Delta V_{tr}$ (cal/mole)	$T \Delta S_{tr}^m$ (cal/mole)	$-\Delta E_{tr}^m$ (cal/mole)
KCl	19.55 ± 0.13	$-62{,}500$	4.11 ± 0.10	1920	0	1920 ± 150
$(K_{0.75}Rb_{0.25})Cl$	15.19 ± 0.19	$+520$	4.46 ± 0.12	1580	-61	1519 ± 250
$(K_{0.50}Rb_{0.50})Cl$	10.50 ± 0.01	$+250$	4.91 ± 0.10	1230	-150	1080 ± 100
$(K_{0.25}Rb_{0.75})Cl$	7.94 ± 0.02	$+269$	5.63 ± 0.07	1080	-144	936 ± 50
RbCl	5.68 ± 0.14	$+357$	6.95 ± 0.11	945	-138	807 ± 150
$K(Cl_{0.75}Br_{0.25})$	20.5 ± 0.2	-730	3.96 ± 0.2	1940	$+39$	1980 ± 300
$K(Cl_{0.50}Br_{0.50})$	20.72 ± 0.14	-650	3.87 ± 0.08	1920	$+40$	1960 ± 150
$K(Cl_{0.25}Br_{0.75})$	19.7 ± 0.2	-1100	3.95 ± 0.2	1860	$+26$	1896 ± 300
KBr	17.99 ± 0.28	-843	4.17 ± 0.11	1790	$+35$	1825 ± 300
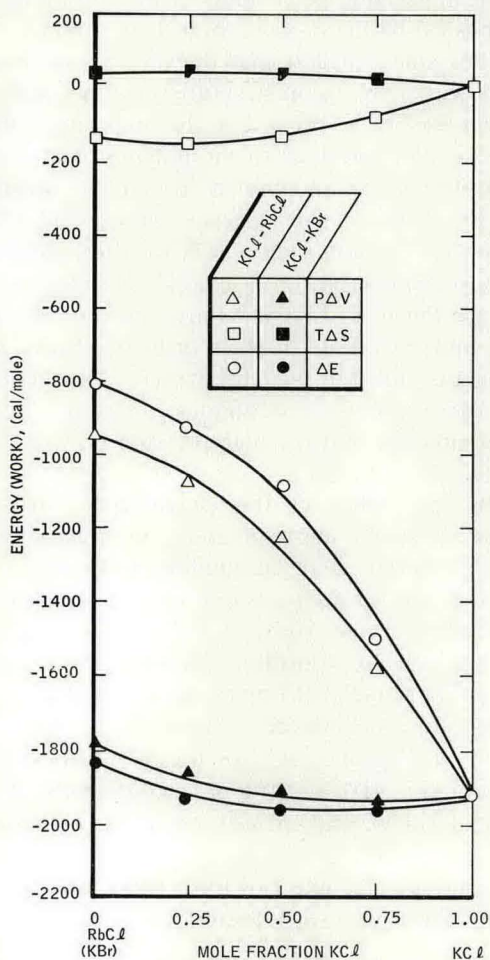
FIG. 7. Variation of $P_{tr}^m \Delta V$, $T \Delta S_{tr}^m$, and ΔE_{tr}^m with mole fraction KCl in the systems KCl–RbCl and KCl–KBr at 298°K.

substitution of Rb^+ for K^+ (cation substitution) or Br^- for Cl^- (anion substitution) is not purely a localized effect around the substituted ion since X-ray diffraction studies show the average interatomic distance is altered by these substitutions. On a mole basis, solvation of RbCl or of KBr increases the lattice parameter of KCl by approximately the same amount. The effect of this cationic and anionic substitution on the properties of this polymorphic transition, is, however, quite different. This can be seen in Figs. 5 and 6 where P_{tr}^m is shown as a function of mole fraction KCl. In Fig. 5 it is seen that complete substitution of Rb^+ for K^+ lowers P_{tr}^m from ~20 kb to ~6 kb. A negative deviation from additivity in P_{tr}^m vs $x(KCl)$ occurs at 200° and at 500°C. At 800°C, however, this relationship between P_{tr}^m and $x(KCl)$ is almost linear. The relationship between P_{tr}^m and $x(KCl)$ in the KCl–KBr system, on the other hand, is essentially independent of $x(KCl)$ and shows a positive deviation from linearity at 500°C (Fig. 6). The curves at 200° and 800°C are similar (and are therefore not shown). It can also be seen from Fig. 3 that substitution of Br^- for Cl^- has very little effect upon ΔV_{tr}, whereas substitution of Rb^+ for K^+ results in an approximately linear increase in ΔV_{tr} from ~4 cm³/mole to ~7 cm³/mole as $x(KCl)$ goes from unity to zero (at 25°C). As might be expected, other thermodynamic properties for this phase transition are also affected to a much greater extent by cationic replacement in comparison to anionic replacement. This can be seen from examination of Fig. 7, where the quantities $P_{tr}^m\Delta V_{tr}$, $T\Delta S_{tr}^m$, and ΔE_{tr}^m for this transition are shown as a function of mole fraction of KCl. The difference in internal energy between a solid solution in the two polymorphic forms is given by $\Delta E_{tr}^m \cong P_{tr}^m\Delta V_{tr} - T\Delta S_{tr}^m$. The internal energy difference for these solid solutions is determined predominantly by $P_{tr}^m\Delta V_{tr}$, since $P_{tr}^m\Delta V_{tr} > T\Delta S_{tr}^m$. Thus both $P_{tr}^m\Delta V_{tr}$ and ΔE_{tr}^m are affected to a much greater extent by cation substitution than by anion substitution. It is noted that cation substitution results in positive deviation, whereas anion substitution shows a corresponding negative deviation from linearity of ΔE_{tr}^m and $P_{tr}^m\Delta V_{tr}$ vs $x(KCl)$. The reverse situation occurs in the $T\Delta S_{tr}^m$ vs $x(KCl)$ curves. We wish to point out that these effects may be a result of the relative sizes of the cations and anions involved in the substitution. For example, in the cationic substitution of Rb^+ for K^+ in the KCl–RbCl system, both cations are smaller than Cl^-; on the other hand, in the anionic substitution of Br^- for Cl^- in the KCl–KBr system, both anions are larger than K^+ (38, 39). In order to further examine the effects of ion size as compared to ionic charge it would be of interest to examine the polymorphic transition in the systems CsF–RbF and CsF–CsCl, where the cation is now the larger ion.

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