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 cm^3/mole to ~ 7 cm^3/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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