

Polymorphism in the KCl-KF and KCl-NaCl Systems at Elevated Pressures and Temperatures*

A. J. DARNELL AND W. A. MCCOLLUM

*Atomics International, A Division of North American Rockwell Corporation,
Canoga Park, California 91304*

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The pressure-induced polymorphic transition in the salt systems KCl-KF and KCl-NaCl was investigated by dilatometry from 25°C to 900°C and at pressures to 50 kb. The transition in these binary systems is similar to the $Fm3m \rightleftharpoons Pm3m$ phase change in KCl. KF does not measurably affect the transition pressure of KCl at any temperature up to 900°. The effect of NaCl upon KCl is also small below 300°. This is understandable because of the low solubility of KF and NaCl (below 300°) in KCl. The transition pressure, (P_{tr}), its width (P_w), and the transition volume (ΔV_{tr}) indicate that the transition observed in the KCl-KF system, and in the KCl-NaCl system at temperatures below 350°, occurs in the KCl-rich phase. However, at temperatures above 350°, NaCl raises P_{tr} , broadens P_w , and decreases ΔV_{tr} . At 800° the elevation in P_{tr} is approximately proportional to mole fraction (X) NaCl. For a given composition, ΔV_{tr} also decreases as T increases. At high T and high X NaCl, $\Delta V_{tr} \rightarrow 0$. The 400°, 500°, 600°, 700°, and 800° isotherms for the P_{tr} vs X NaCl curves were extrapolated to X NaCl = 1. This procedure yields hypothetical P_{tr} vs T and ΔV_{tr} vs T curves for this polymorphic transition in pure NaCl. This extrapolation indicates that for pure NaCl $\Delta V_{tr} = 0$ at 300°; $\Delta V_{tr} > 0$ when $T < 300^\circ$. At 300° the extrapolated value of P_{tr} is 14 kb. These curves aid in understanding the conflicting reports for a polymorphic transition in pure NaCl in the pressure range of 12–30 kb.

I. INTRODUCTION

It is well known that the alkali halides occur in two crystal modifications: the "rock salt" form, space group $Fm3m$, and the CsCl form, space group $Pm3m$. Polymorphism between these two structure types is known to take place in over half of these compounds.¹

This group of salts offers a good opportunity for examination of atomic or periodic trends in properties of ionic compounds, particularly of the phase transition between these two relatively simple cubic modifications, $Fm3m$ and $Pm3m$. Indeed, a regular variation in the fusion properties of the $Fm3m$ form of these salts with interatomic spacing (or mean distance of closest approach of ions in the solid phase) is known (7).

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¹ The literature on the phase transitions in this class of compounds is extensive. For further information the reader is referred to papers by Tosi and Fumi (1), Schumacher (2), Tosi (3), Klement and Jayaraman (4), and Darnell and McCollum (5, 6).

In a previous paper Darnell and McCollum (5) have examined the polymorphic transition in the potassium and rubidium halides from room temperature to temperatures near the triple point, $Fm3m \rightleftharpoons \text{liquid} \rightleftharpoons Pm3m$. In a subsequent paper these authors have made a similar study of the polymorphic transition in the binary solid solutions of the system KCl-KBr and KCl-RbCl (6). The first of these salt systems illustrates the effects of anionic substitution (Br^- for Cl^-), the latter cationic substitution (Rb^+ for K^+), upon this polymorphic transition. This paper is a continuation of the study of the effects of ionic substitution upon this polymorphic transition. Here we examine the effects of ionic substitution upon the $Fm3m \rightleftharpoons Pm3m$ transition in KCl through study of the systems KCl-KF and KCl-NaCl.

II. EXPERIMENTAL

A. Materials

The salts KCl, NaCl, and KF used in this work were Mallinckrodt analytical reagent grade. The procedures used for drying these salts and the preparation of their solid solutions or mixtures are described elsewhere (5, 6). In the binary systems studied in an earlier work (6) the salts RbCl and KBr formed continuous solid solutions with KCl, even at room temperature. NaCl, however, is completely miscible with KCl only at temperatures above 500° (8, 9, 10, 11). X-Ray diffraction measurements made at ambient temperature and pressure of samples prepared for these phase transition studies show essentially pure phases of the component salts. These diffraction measurements were made upon samples which had been heated at 250° for several hours. Metastable solid solutions of KCl and NaCl can be obtained, however, at room temperature by a quench process (11). In the KCl-KF system, KF is only very slightly soluble in KCl at room temperatures (12); its solubility in KCl at high temperatures is not known. Samples of KCl-KF and KCl-NaCl were heated at 250° for at least an hour within the high-pressure apparatus (at a pressure of ~ 2 kb) before carrying out the phase transition studies upon them.

B. Apparatus and Procedure

These phase transition studies were carried out utilizing a piston-cylinder apparatus. The salt sample or pellet was heated by a graphite furnace within the high-pressure chamber. A piston displacement method was used for detection of the polymorphic change and the measurement of the transition volume. This apparatus and technique are similar to those employed by Darnell and McCollum in their study of the polymorphic transition in KCl, RbCl, KBr, KCl-RbCl, and KCl-KBr (5, 6). Sample temperatures were determined from a thermocouple placed within the salt sample in the high-pressure chamber (5). No correction has been made for the effect of pressure upon the thermocouple emf. This pressure effect is, however, small (i.e., less than 1%) for chromel-alumel junctions at pressures below 25 kb.

III. RESULTS

A. KCl-KF

Mixtures with the compositions 90 mole % (m/o) KCl and 75 m/o KCl were examined at approximately 100° intervals from room temperature to 900° over the