

system, similar to Bassett's (17) phase studies using high-pressure X-ray diffraction upon pure NaCl, is needed.

We wish to point out the rather surprising implications which one might anticipate for the transition in pure NaCl based upon extrapolation of the  $P_{tr}^m$  vs  $X$  (NaCl) (Fig. 1) and  $\Delta V_{tr}$  vs  $X$  (NaCl) (Fig. 3) to the composition of pure NaCl. Such extrapolated values of  $P_{tr}^m$  and  $\Delta V_{tr}$  from several of the isotherms are shown in Fig. 4.

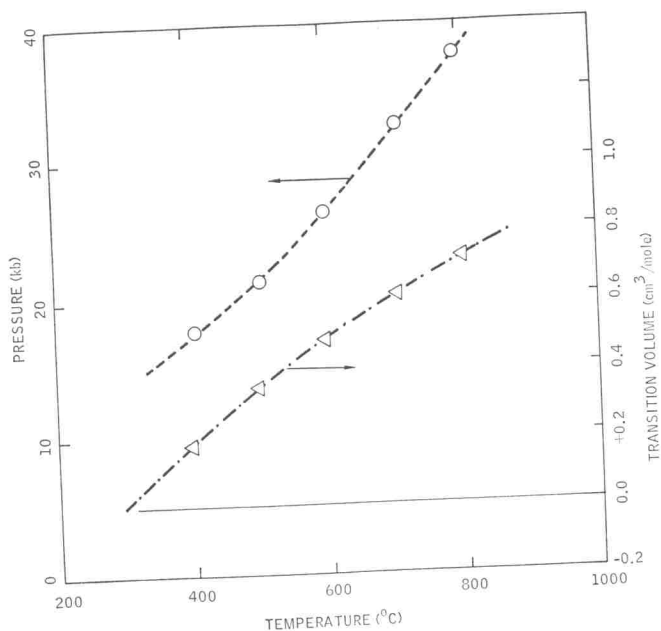


FIG. 4. Transition pressure ( $P_{tr}^m$ ) and transition volume ( $\Delta V_{tr}$ ) obtained from extrapolation of the curves  $P_{tr}^m$  vs  $X$  (NaCl) and  $\Delta V_{tr}$  vs  $X$  (NaCl) to  $X$  (NaCl) = 1 at the isotherms 400°–800°.

It is interesting to note that the extrapolated value for  $\Delta V_{tr}$  is positive for this pressure-induced transition at temperature above 300°. Therefore this hypothetical curve for NaCl predicts, for thermodynamic reasons, that no polymorphic transition of this type is possible between 300° and 800°. These hypothetical curves suggest that some transition phenomena may be occurring in NaCl at temperatures below 300° in the pressure range of 15 kb which may be connected with the transitions reported by Evdokimova and Vereshchagin (18), Larson (19), and by Pistorius (20) for NaCl.

## V. CONCLUSIONS

### A. KCl-KF

It is not possible to examine the effect of anionic substitution of  $F^-$  for  $Cl^-$  upon the polymorphic transition in KCl because of the limited solid solubility of these two salts even at temperatures approaching the melting curve.

B. *KCl-NaCl*

At elevated temperatures ( $> 600^\circ$ ) where NaCl becomes completely miscible in KCl, the cationic substitution of  $\text{Na}^+$  for  $\text{K}^+$  raises the polymorphic transition pressure ( $P_{\text{tr}}^m$ ) of KCl in an almost linear fashion (as a function of m/o NaCl). On the other hand, this cationic substitution lowers the polymorphic transition volume ( $\Delta V_{\text{tr}}$ ). A distinct trend is seen from comparison of the results from this study with the results from a similar study by Darnell *et al.* (6) on the KCl-RbCl system; viz., substitution of the larger  $\text{Rb}^+$  ion in KCl lowers the polymorphic transition pressure ( $P_{\text{tr}}^m$ ) but increases the transition volume ( $\Delta V_{\text{tr}}$ ). In contrast, the reverse effect is noted in  $P_{\text{tr}}^m$  and  $\Delta V_{\text{tr}}$  upon the substitution of the smaller  $\text{Na}^+$  cation in KCl. In particular, it is noted in the KCl-NaCl system that  $\Delta V_{\text{tr}} \rightarrow 0$  when  $X(\text{NaCl}) \rightarrow 1$ . Thus for thermodynamic reasons, the pressure induced polymorphic transition in solid solutions of KCl-NaCl fails to occur at high concentrations of NaCl. These results give some clue or explanation why a transition is not observed in NaCl in the pressure region of 15–30 kb, such as is observed in the case of RbCl at a pressure of 5 kb and in KCl at 20 kb. NaCl behaves much differently from the latter two salts in its  $Fm3m \rightleftharpoons Pm3m$  transition. Such a transition has been observed in NaCl by Bassett and Takahashi (17) at a much higher pressure of 300 kb. At this extreme pressure the volume change for this  $Fm3m \rightarrow Pm3m$  transition in NaCl behaves in a normal manner.

## REFERENCES

1. TOSI, M. P. AND FUMI, F. G., *J. Phys. Chem. Solids* **23**, 359 (1962).
2. SCHUMACHER, D. P., *Phys. Rev.* **126**, 1679 (1962).
3. TOSI, M. P., in "Solid State Physics" (F. Seitz and D. Turnbull, Eds.), Vol. 16, Academic Press, New York, 1965.
4. KLEMENT, W. AND JAYARAMAN, A., in "Progress in Solid State Chemistry" (H. Reiss, Ed.), Vol. 3, Pergamon Press, Oxford, 1966.
5. DARNELL, A. J. AND MCCOLLUM, W. A., *J. Phys. Chem. Solids* **31**, 805 (1970).
6. DARNELL, A. J. AND MCCOLLUM, W. A., *High Temp. Sci.* **2**, 331 (1970).
7. BAUER, S. H. AND PORTER, R. F., in "Molten Salt Chemistry" (M. Blander, Ed.), p. 623, Wiley (Interscience), New York, 1964.
8. LEVIN, E. M., ROBBINS, C. R., AND MCMURDIE, H. F., "Phase Diagram for Ceramists," p. 376, American Ceramic Society, Columbus, Ohio, 1964.
9. SCHEIL, E. AND STADELMAIER, H., *Z. Metallk.* **43**, 227 (1952).
10. BUNK, A. J. H. AND TICHELAAR, G. W., *Verh. Kon. Ned. Akad. Wetensch., Ser. B* **56**, 378 (1953).
11. BARRETT, W. T. AND WALLACE, W. E., *J. Amer. Chem. Soc.* **76**, 366 (1954).
12. Reference (8), p. 455.
13. PIERMARINI, G. J. AND WEIR, C. E., *J. Chem. Phys.* **37**, 1887 (1962).
14. PISTORIUS, C. W. F. T. AND SYNMAN, H. C., *Z. Phys. Chem. Neue Folge* **43**, 1 (1964).
15. PISTORIUS, C. W. F. T., *J. Phys. Chem. Solids* **26**, 1543 (1965).
16. JAMIESON, J. C., in "Physics of Solids at High Pressure" (C. T. Tomizuka and R. M. Emrick, Eds.), pp. 444–458, Academic Press, New York, 1965.
17. BASSETT, W. A., TAKAHASHI, T., MAO, H., AND WEAVER, J. S., *J. Appl. Phys.* **39**, 319 (1968).
18. EVDOKIMOVA, V. V. AND VERESHCHAGIN, L. F., *Fiz. Tverd. Tela* **4**, 1965 (1962).
19. LARSON, D. B., Ref. (16), p. 459.
20. PISTORIUS, C. W. F. T., *J. Phys. Chem. Solids* **25**, 1477 (1964).