

and due to thermal vibrations are calculated correctly or result erroneously in two solubility gaps.

Table 3. Maximum temperature T_m (in °K) of the exsolution dome, temperature difference ΔT (in °K) between the chemical and the coherent spinodal, maximum temperature T_{coh} of the coherent spinodal, and elastic anisotropy α at the maximum of the chemical spinodal for several pressures (in kbar)

System	p	T_m	ΔT	T_{coh}	α
LiBr-LiI	0	575	269	306	-0.64
	50	1010	241	769	0.19
	100	1080	225	855	1.39
NaBr-NaI	0	665	324	341	-0.18
	5	705	345	360	-0.003
	10	750	369	381	0.156
	50	880	467	413	1.55
KBr-KI	100	900	591	309	2.87
	0	520	215	305	1.36
	10	615	182	433	2.72
RbBr-RbI	20	690	158	532	4.44
	0	515	183	332	1.87
	2	538	172	365	2.26
NaCl-KCl	4	560	162	398	2.69
	0	883	487	396	-0.29
	10	980	552	428	0.10
	20	1077	515	562	0.51

The parameters used in the present calculations that determine the pressure dependence of the solid solubility curve are the compressibilities and the electronic polarizabilities, the first pressure derivatives of these quantities, and the lattice parameters. It is still conceivable, however, that the solid solubility and its pressure dependence can be correlated to a smaller number of parameters. Such a correlation would be useful for more complicated systems where lattice theoretical calculations are too difficult. One such 'empirical' correlation of the theoretical results is plotted in Fig. 6, which shows the ratio of the maximum temperature of the exsolution dome $T_m(p)$ at the pressure p to the maximum temperature $T_m^0 = T_m(0)$ at

zero pressure as a function of $(V_0/V)^{4/3}$, where V and V_0 are the molar volumes (corresponding to the composition of the maximum of the exsolution dome) at pressure p and at zero pressure, respectively. For all four systems a linear correlation is found for values of $(V_0/V)^{4/3}$ close to 1, i.e. for small pressure. For LiBr-LiI and NaBr-NaI deviations from the linear dependence occur at higher values of $(V_0/V)^{4/3}$. For these two systems the cation-anion radius ratio r_+/r_- is smaller or close to the value $(\sqrt{2}-1) = 0.41$ below which the repulsive interaction between second nearest neighbors becomes more pronounced than that between first nearest neighbors. Although because of the occurrence of the B1-B2 phase transition the data for KBr-KI and RbBr-RbI have not been extended to higher pressures to allow a comparison, it is conceivable that the deviation from linearity in Fig. 6 is associated with the small cation anion radius ratio. This behavior warrants further study, especially for other systems. Apart from this observation, no other effect of the radius ratio on solid solubility could be found.

The only experimental data on the pressure dependence of the solid solubility in alkali halides that are available for comparison with the theoretical results are recent and as yet unpublished results of Bhardwaj and Roy for the system NaCl-KCl[33]. The solid solubility curve at zero pressure found by these authors agrees well with the earlier data of Sheil and Stadelmaier[45] and lies therefore about 100°C below our theoretical curve (II, Fig. 3). Possible reasons for this discrepancy have been discussed in II. Good agreement between the theoretical and experimental results is found, however, for the pressure dependence of the solid solubility; the experimental and theoretical curves for the maximum of the exsolution dome vs. pressure have the same shape and differ only by a parallel shift of about 100°C[33]. This pressure dependence corresponds therefore to the linear dependence of the maximum

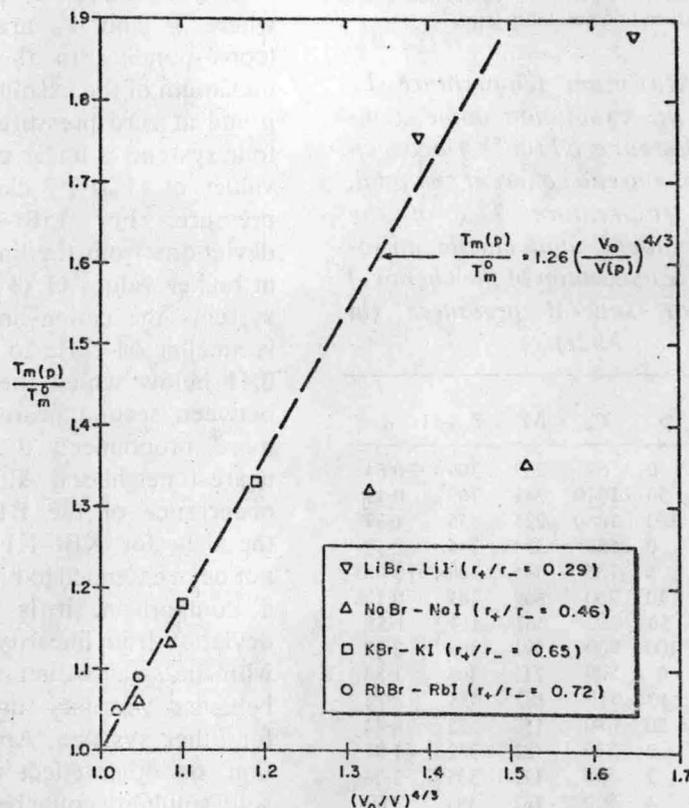


Fig. 6. Dependence of maximum temperature of exsolution dome on volume for several pressures and several systems.

of the exsolution dome on the volume ratio $(V_0/V)^{4/3}$ displayed in Fig. 6.

4. CONCLUSIONS AND SUMMARY

It is found that for all alkali halide systems considered the solid solubility curve becomes narrowed and is shifted toward higher temperatures as the pressure increases. A similar behavior is found for the chemical spinodal. The increase with pressure results primarily from the increase of the heat of formation through the decreasing interionic distance. The temperature difference between the chemical and the coherent spinodal does not follow a general pattern and may either increase monotonously, decrease monotonously, or decrease at high pressure after initially at low pressures passing through a maximum.

For all five systems considered the coherent spinodal at zero pressure does not rise very much above 300°K, but of these systems NaCl-KCl is most likely to show spinodal decomposition at 300°K and zero pressure. In most cases the maximum temperature of the coherent spinodal increases with increasing pressure, so that, for example, for KBr-KI spinodal decomposition is expected to occur at 10 kbar over a certain composition range. For NaCl-KCl a similar behavior is expected, but the increase with pressure occurs more slowly, and pressures of the order of 20 kbar are required to raise the coherent spinodal significantly above the zero pressure value.

For LiBr-LiI, NaBr-NaI and NaCl-KCl the direction in which spinodal decomposition occurs changes with pressure because the elastic anisotropy changes sign