equation (2.1) in connection with the assumptions stated in Section 2 and the methods used in I for calculating Q_F and ΔS. Figures 1–4 show the solid solubility curves (exsolution domes) and the chemical spinodals for the systems LiBr–LiI, NaBr–NaI, KBr–KI, and RbBr–RbI. In addition, the solid solubility curves were calculated for NaCl–KCl at two pressures and are shown in Fig. 5. The systems chosen were selected in view of the possibility of detecting any effect of increasing cation size on solid solubility and its pressure dependence. The system NaCl–KCl was added since an experimental determination of the pressure dependence of the solid solubility was started in this laboratory while the present theoretical work was in progress[33].

With the exception of the system NaBr–NaI all pressures selected for the solid solubility curves are smaller than the transition pressures for the transition from the NaCl to the CsCl structure. For the Li-halides no transition has been observed so far. Theoretical estimates for LiBr and LiI have been made on the basis of the Born model[34] and give 105 and 68 kbar, respectively. Quantum theoretical calculations[35] give 140 and 67 kbar, respectively. For NaBr and NaI the theoretical values from the Born model[34] are 53 and 39 kbar respectively, and from quantum theory[35] 78 and 44 kbar, respectively. Pistorius, however, observed the transition in NaBr at 11.5 kbar and 200°C, and in NaI at 10.2 kbar and 164°C[36]. At room temperature no transition was observed. These results are, however, subject to doubt because of the large discrepancies between the experimental and the quantum theoretical results, and because the theoretical results show a tendency for the transition pressure to increase in the sequence rubidium, potassium and sodium halides. In fact, for the potassium and rubidium halides the quantum theoretical calculations agree quite well with the available experimental data which indicate transition pressures near 4 kbar for the rubidium halides, and near 18 kbar for the potassium halides[35, 36].

Moreover, a large discrepancy exists among the transition pressures reported for NaCl by various investigators, and the low transition pressure for NaCl of 18 kbar found by Pistorius[37] has been challenged by Basset *et al.* [38], who propose a transition pressure of 300 kbar for NaCl. In view of these arguments it is conceivable that the transition pressures near 10 kbar reported by Pistorius [36] for NaBr and NaI are also much too low, and that the true transition pressures for these materials may well be near or above 100 kbar.

For these reasons the solid solubility curves of the system NaBr–NaI were calculated for two different sets of pressure, one set (5 and 10 kbar) below the

transition pressure reported by Pistorius[36], and one set (50 and 100 kbar) in a pressure range in which this system possibly (i.e. if Pistorius' data should turn out to be due to secondary effects) still occurs in the rocksalt structure.

For KBr and KI the transition occurs at 17.4 and 17.3 kbars respectively[36], so that the highest pressure for the KBr–KI diagram in Fig. 3 lies slightly outside the stability range of the rocksalt structure. For RbBr and RbI the experimental transition pressures are 4.2 and 3.6 kbars, respectively[36], so that the solubility curve at 4 kbar shown in Fig. 4 lies slightly outside the stability range of the rocksalt phase.

The results displayed in Figs. 1–5 show that for all five systems considered the exsolution domes become narrower and their maxima are moved toward higher temperatures with increasing pressure, while for a given temperature the solubility gap increases with increasing pressure. This indicates that the effect of pressure on solid solubility is opposite to the effect of temperature. This is what one would expect intuitively. Upon application of pressure, the ions are moved in their potential wells toward the high repulsive core making them effectively 'harder'. This reduces the possibility for accommodating misfits. Hence, increasing the pressure decreases the solid solubility, while an increase in temperature increases the solid solubility.

For the system LiBr–LiI in Fig. 1 the exsolution domes for pressures of 50 and 100 kbar extend above the approximate melting temperature curve, so that at those pressures, it is not possible to have complete solid solubility over the whole composition range.

The chemical spinodals shown in Figs. 1–4 exhibit the same pressure dependence as their respective solid solubility curves. The area under the chemical spinodal increases with increasing pressure. This means that the range in which the solid solution would decompose by spinodal decomposition in the absence of the strain term is increased both in temperature and in composition.

The temperature difference ΔT between the chemical and coherent spinodals was calculated (from equation (2.8)) at the maximum
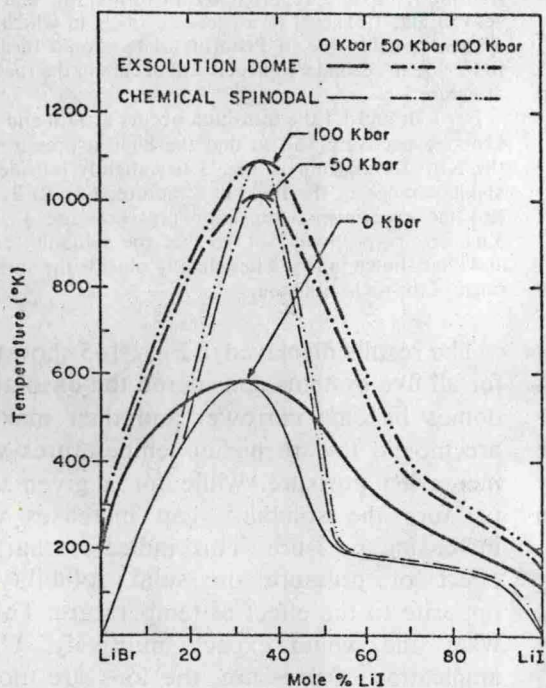
Fig. 1. Exsolution dome and chemical spinodal of LiBr–LiI for three pressures.

Fig. 2(a). Exsolution dome and chemical spinodal of NaBr–NaI for several pressures.

of the exsolution dome for the five systems under investigation. In order to calculate Y (in 2.6) the elastic constants were evaluated at the proper temperature, pressure, and composition. The pressure data were those of Table 1, while the values for the temperature dependence of the elastic constants were taken from the compilation of Leibfried and Ludwig[39]. The zero pressure values of the molar volumes were calculated from the lattice constants compiled[40]. The values of the maximum temperature T_m of the exsolution dome, for the maximum temperature $T_{coh} = T - \Delta T$ of the coherent spinodal, and of the temperature difference ΔT are listed in Table 3 for several pressures. Also included in Table 3 are the values of the anisotropy factor (2.5).

The values of T_{coh} listed in Table 3 represent an estimate of the temperature below which one might observe spinodal decomposition for each alkali halide solid solution, assuming the coherent spinodal is properly
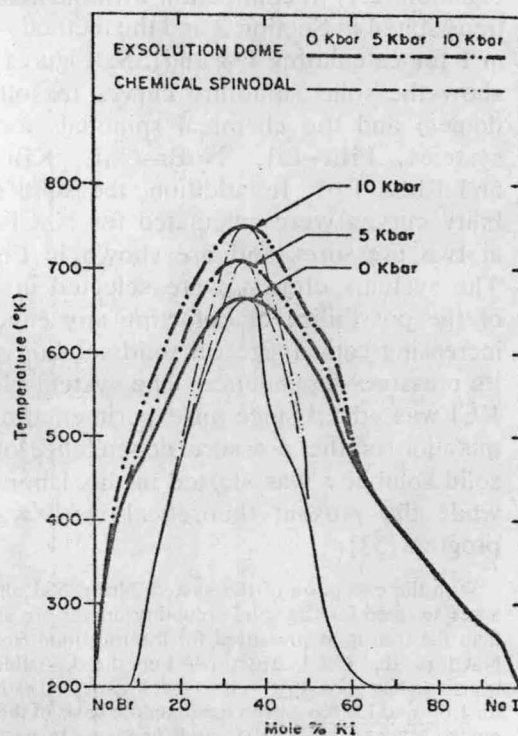
calculated. However, the strain term, given by equation (2.4) and the method outlined for relating the strain term to the temperature drop given by (2.8) are both approximate enough to make one cautious about drawing quantitative conclusions about the temperature differences between the chemical and coherent spinodals.

With these reservations in mind one may observe from the data of Table 3 that for all systems, except NaBr–NaI, the maximum temperature T_{coh} of the coherent spinodal increases monotonically with pressure. For NaBr–NaI, however, the temperature T_{coh} increases initially and decreases at high pressure after passing through a maximum. This maximum is caused by the fact that for NaBr–NaI the temperature difference ΔT between the chemical and the coherent spinodal increases with pressure, whereas for LiBr–LiI, KBr–KI, and RbBr–RbI, ΔT decreases with increasing pressure. For