

LATTICE THEORY OF ALKALI HALIDE SOLID SOLUTIONS—III. PRESSURE DEPENDENCE OF SOLID SOLUBILITY AND SPINODAL DECOMPOSITION*

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(Received 30 April 1970)

Abstract—The solid solubility and the chemical spinodal have been calculated for several pressures from an extended theory of the authors based on the substitutional defect model of Dick and Das. The systems considered are LiBr–LiI, NaBr–NaI, KBr–KI, RbBr–RbI, and NaCl–KCl. The maxima of the exsolution dome, of the chemical spinodal and of the coherent spinodal are found to increase and to become narrowed with increasing pressure. For three systems the temperature difference between the chemical and the coherent spinodal decreases with increasing pressure, for one system it increases, and for the remaining system it increases initially with increasing pressure and decreases after passing through a maximum. The direction in which spinodal decomposition should occur is found to be dependent on pressure for several systems.

I. INTRODUCTION

IN TWO previous papers [1, 2] (referred to as I and II) the authors have investigated the heat of formation, the entropy of mixing and the solid solubility of alkali halide solid solutions on the basis of an extension of the substitutional defect model of Dick and Das [3]. While this earlier work was restricted to zero pressure, it is the objective of the present paper to extend the previous work to investigate theoretically the pressure dependence of solid solubility for several alkali halides and to determine the effect of pressure on spinodal decomposition.

A study of solid solubility at high pressure is relevant for several reasons. First, it is of interest to investigate whether the effect of thermal motion and of external pressure

act, as is usual for many physico-chemical properties in opposite directions. In the absence of any experimental data for alkali halides this question cannot be answered beforehand because the elastic shear constants determine the solid solubility curve and the coherent spinodal via the vibrational contribution to the entropy of mixing, and through the strain term, respectively, and because for some alkali halides the pressure derivative of the shear constant c_{44} is negative (See e.g. the compilation in [4]).

The pressure dependence of solid solubility is also of interest in geophysics. For example, in determining the composition of the core of the earth the solubility of the main constituent of the mantle, olivine ((Mg, Fe)₂SiO₄) in the iron-rich core must be known in the megabar range [5]. Although the two systems are very different one would hope that the present work on alkali halides may serve as a first step towards the study of more complicated systems.

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Finally, the decomposition of solid solutions, especially through the spinodal mechanism, has recently been utilized for the preparation of multiphase and high-strength materials [6-8], and it is conceivable that the application of pressure as an additional parameter will be useful for materials engineering.

Spinodal decomposition was first predicted from thermodynamic principles by Gibbs [9]. It consists of a mechanism for the decomposition of solid solutions which occurs in that region of the p - T - x phase diagram in which the second derivative of the Gibbs free energy with respect to composition is negative. While for metals [10], glasses [11] and ionic materials [12] the occurrence of spinodal decomposition has been confirmed experimentally, it is still uncertain, however, whether or not observed phase separations in alkali halides are due to the spinodal mechanism [13-15]. This lack of understanding has in part motivated the present study. It is hoped that the theoretical results obtained will stimulate further experimental work in this area. Perhaps a crucial experiment may be designed by introducing pressure as an additional variable, or the interpretation of new experimental data may be facilitated, so that it will be possible to determine whether the spinodal mechanism is active or not.

2. METHOD AND ASSUMPTIONS

The solid solubility curves at non-zero pressure are determined by the free energy function

$$G^* = Q_F - T\Delta S + p(V_{SS} - V_M) \quad (2.1)$$

where Q_F is the heat of formation, ΔS is the total entropy of solution, V_{SS} and V_M are the volumes of the solid solution and mechanical mixture, respectively, and p and T are the pressure and temperature respectively. All extensive quantities will be referred to one mole throughout this paper. The solid solubility curve can be calculated from the free energy function (2.1) by the method of equal tangents [16].

The chemical spinodal is the boundary between the two regions in which the crystal should decompose theoretically either by classical nucleation (metastable region) or by spinodal decomposition, commonly referred to as nonclassical nucleation (unstable region). The chemical spinodal is defined as the locus of points for which

$$\frac{\partial^2 G^*}{\partial x^2} = 0 \quad (2.2)$$

where G^* is the free energy function and x represents the composition in mole fractions of one of the components. Cahn [17, 18] has introduced another spinodal, called the coherent spinodal, which is defined by

$$\frac{\partial^2 G^*}{\partial x^2} + W = 0 \quad (2.3)$$

and which should describe the spinodal observed experimentally. The 'strain term' W takes into account the elastic strain associated with the decomposition. This strain term is positive and causes a lowering of the chemical spinodal, i.e. it enhances the stability of the solid solution by increasing the metastable region and decreasing the unstable region. For cubic crystals the strain term is given by [18]

$$W = 2\eta^2 Y \quad (2.4)$$

where $\eta = (1/r)(\partial r/\partial x)$ is the derivative of the nearest neighbor distance in the solid solution with respect to composition, and Y is an orientation dependent elastic coefficient. Spinodal decomposition occurs in the direction for which the coefficient Y has a minimum, which corresponds to $\langle 100 \rangle$ for $\alpha < 0$ and $\langle 111 \rangle$ for $\alpha > 0$ where

$$\alpha = \frac{c_{11} - c_{12} - 2c_{44}}{2c_{44}} \quad (2.5)$$

is the elastic anisotropy factor. The corre-

sponding minimum values of the coefficient Y are [18]

$$Y = \begin{cases} (C_{11} + 2c_{12})(c_{11} - c_{12})/c_{11} & (\alpha < 0) \\ 6(c_{11} + 2c_{12})c_{44}/(c_{11} + 2c_{12} + 4c_{44}) & (\alpha > 0). \end{cases} \quad (2.6)$$

The temperature difference $\Delta T = T_s - T_{s'}$ between the chemical and coherent spinodals (T_s and $T_{s'}$, respectively) may be according to Hilliard[19] approximately written as

$$\Delta T = T_s - T_{s'} = -2\eta^2 Y / \left(\frac{\partial^2 \Delta S}{\partial x^2} \right). \quad (2.7)$$

If ΔS is assumed to consist of the entropy of ideal mixing only [20, 2] equation (2.7) becomes

$$\Delta T = \frac{2\eta^2 Y}{kN_0} x(1-x) \quad (2.8)$$

where k is Boltzmann's constant and N_0 is the number of molecules per unit volume.

The composition dependence of the heat of formation and of the solid solubility were calculated for several pressures in the same manner as in I and II, but with (2.1) as free energy function, and with Q_F , ΔS , V_{ss} and V_M occurring in (2.1) dependent on pressure. As in I and II, the heat of formation has been assumed to be independent of temperature. The pressure dependence of Q_F results from the pressure dependence of the nearest neighbor distance and of the electronic polarizabilities. The pressure dependence of the nearest neighbor distance was calculated from the isothermal bulk modulus and its isothermal pressure derivative obtained from the data presented in Table 1 by using Murnaghan's equation of state[21]. The pressure dependence of the polarizabilities was calculated from the available experimental data of the pressure dependence of the refractive index[30-32] by assuming that the electronic polarizabilities of cations and anions are additive.

Table 1. Isothermal elastic constants (in 10^{11} dynes/cm²) and their isothermal pressure derivatives for several alkali halides

	c^T	c_{12}^T	c_{44}	$(\partial c_{11}^T / \partial p)_T$	$(\partial c_{12}^T / \partial p)_T$	$(\partial c_{44}^T / \partial p)_T$
LiBr	3.74[a]	1.67	1.93	8.02[h]	2.20	0.19
LiI	2.64[b]	0.78	1.35	9.60[h]	2.07	0.09
NaBr	3.82[c]	0.958	1.015	11.04[i]	1.80	0.423
NaI	2.93[d]	0.807	0.742	11.85[d]	2.36	0.584
KBr	3.35[e]	0.450	0.508	13.03[j]	1.66	-0.328
KI	2.62[e]	0.344	0.369	13.93[j]	2.36	-0.241
RbBr	3.10[f]	0.404	0.383	13.43[f]	1.38	-0.54
RbI	2.52[f]	0.322	0.279	13.64[f]	1.45	-0.50
NaCl	4.77[g]	1.13	1.27	11.74[g]	2.16	0.37
KCl	3.97[g]	0.615	0.630	12.89[g]	1.67	-0.385

[a] Calculated from adiabatic data of Haussühl[22].

[b] Calculated from adiabatic data of Haussühl[23].

[c] Koliwad *et al.*[24].

[d] Barsch and Shull[25].

[e] Reddy and Ruoff[26].

[f] Chang and Barsch[27].

[g] Bartels and Schuele[28].

[h] Theoretical data by Ghate[29] (Table 4, repulsive parameter $b = 0.333$).

[i] Calculated from the isothermal derivatives of the adiabatic elastic constants of Koliwad *et al.*[24].

[j] Calculated from the isothermal derivatives of the adiabatic elastic constants of Reddy and Ruoff[26].

The volume of the solid solution, V_{ss} , is calculated by assuming Vegard's law for the nearest neighbor distance of the solid solution, i.e. a linear variation with composition. Even though the individual volumes, V_{ss} and V_M , are temperature-dependent, the difference ($V_{ss} - V_M$) is assumed to be independent of temperature*, but dependent on pressure according to Murnaghan's equation of state. Below 100 kbar, the work term, $p(V_{ss} - V_M)$, in (2.1) amounts only to less than about 10 per cent of the heat of formation, so that neglecting the temperature dependence of this term is not critical.

The total entropy of solution consists of two parts, the entropy of ideal mixing, ΔS^{id} , and the vibrational contribution, ΔS^{vib} , as explained in II. The term, ΔS^{vib} , is assumed to be independent of temperature. Calculations were made to test this assumption about ΔS^{vib} and it was found that ΔS^{vib} was essentially independent of temperature. The pressure dependence of the vibrational contribution to the entropy was, however, taken into account through the pressure dependence of the constant A occurring in the formula for the composition dependence of the elastic constant c_{11} II:

$$\Delta c_{11} = Ax(1-x) \quad (2.9)$$

Δc_{11} is the difference between the elastic constant of the solid solution and that of the

solid mixture, and A depends on the molar volumes and the bulk moduli of the two end members of the solid solution series (equations (2.8) and (2.13) of II), which are here considered as pressure-dependent according to Murnaghan's equation of state, and according to the linear pressure dependence of the elastic constants, respectively. For the alkali halide systems contained in Table 1 the constant A and the relative deviation $\Delta c_{11}/c_{11}^{Mix}$ of the elastic constant c_{11} in the solid solution from the value in the solid mixture are for a composition $x = 0.5$ presented in Table 2 for several pressures.

3. RESULTS AND DISCUSSION

Solid solubility curves and chemical spinodals were calculated for five alkali halide systems for several pressures from

Table 2. The quantity A (in 10^{11} dynes/cm²) defined in equation (2.9) and the predicted relative deviation (in per cent) of the elastic constant c_{11} for the solid solution from the value for the solid mixture at $T = 300^\circ\text{K}$ and at the composition $x = 0.5$ for several pressures p (in kbar)

System	p	A	$\frac{\Delta c_{11}(0.5)}{c_{11}^{Mix}(0.5)}$
LiBr-LiI	0	-2.514	-19.7
	50	-0.887	-2.9
	100	-0.439	-0.91
NaBr-NaI	0	-0.587	-4.3
	5	-0.476	-3.01
	10	-0.390	-2.16
	50	-0.055	-0.15
KBr-KI	100	+0.139	+0.23
	0	-0.444	-3.7
	10	-0.233	-1.3
RbBr-RbI	20	-0.124	-0.55
	0	-0.314	-2.8
	2	-0.293	-2.4
NaCl-KCl	4	-0.275	-2.1
	0	-1.225	-7.0
	10	-1.048	-4.7
	20	-0.935	-3.4

*As the reviewer has kindly suggested it would have been easy to take into account the temperature dependence of the term $\Delta V = V_{ss} - V_M$ in an approximate manner by assuming, e.g. the ratio $\Delta V/\bar{V}$ to be temperature independent, so that ΔV has the same thermal expansion as $\bar{V} = (V_{ss} + V_M)/2$. This improvement would have increased the work term $p\Delta V$ by about 5 to 10 per cent, and the total Gibbs free energy by about 0.5 to 1 per cent, at the highest pressures considered, and at temperatures corresponding to the maximum of the exsolution dome. At lower pressures and/or temperatures the change would be proportionally smaller. It is therefore safe to assume that the resulting changes would be barely noticeable in Figs. 1-5. It would be desirable, however, to have this effect included in any future calculations.

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

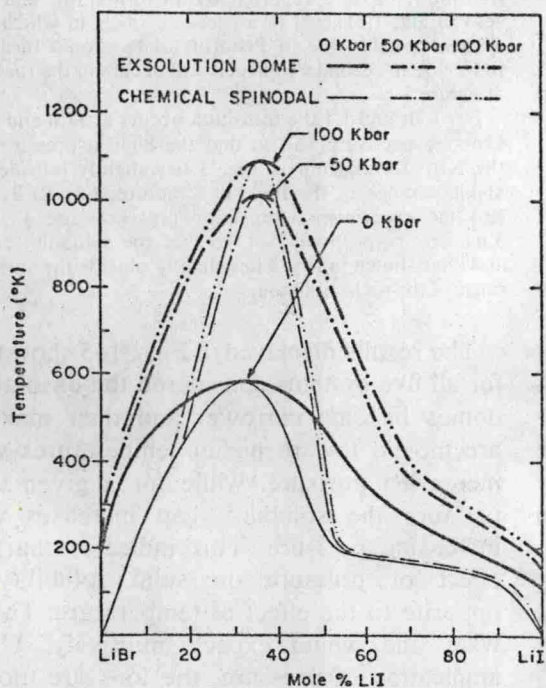


Fig. 1. Exsolution dome and chemical spinodal of LiBr-LiI for three pressures.

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

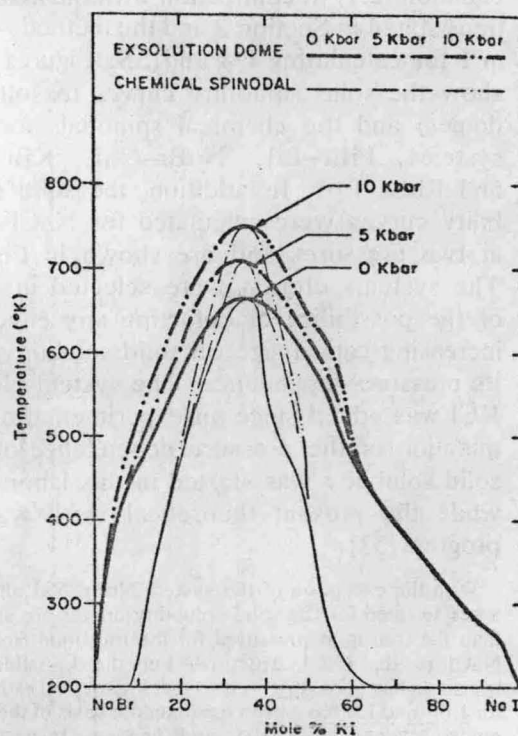


Fig. 2(a). Exsolution dome and chemical spinodal of NaBr-NaI for several pressures.

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

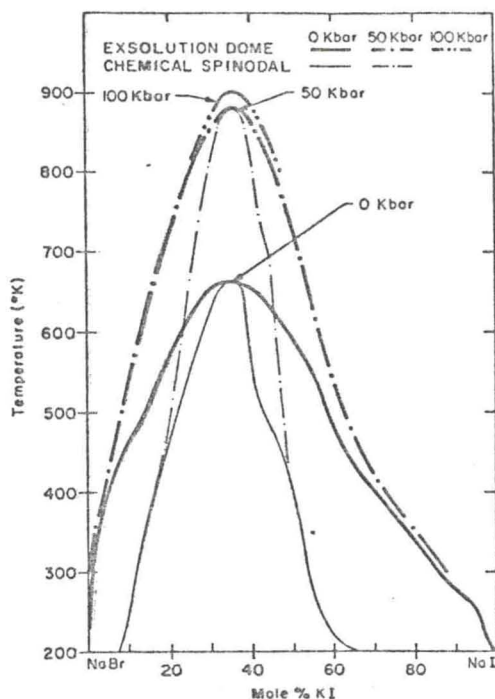


Fig. 2(b). Exsolution dome and chemical spinodal of NaBr-NaI for zero pressure and for two pressures above the transition pressure.

NaCl-KCl the difference ΔT increases initially and decreases after passing through a maximum; however, the initial increase is not large enough to cause a decrease in the maximum temperature T_{coh} .

The different pressure dependence of the temperature difference ΔT arises from the competing effects of the pressure dependence of the different factors (equation (2.8)). The elastic modulus Y usually increases monotonically with pressure, except for KBr-KI and RbBr-RbI, where a maximum occurs near 15 and 2 kbar, respectively. These maxima are caused by the negative pressure coefficient of the shear modulus c_{44} , but since they are very broad they have no effect on the temperature difference ΔT which for these two systems decreases monotonically with pressure. The factor η decreases monotonically with pressure, except for NaBr-NaI, where a minimum occurs, which has, however, no effect on the monotonical increase of the

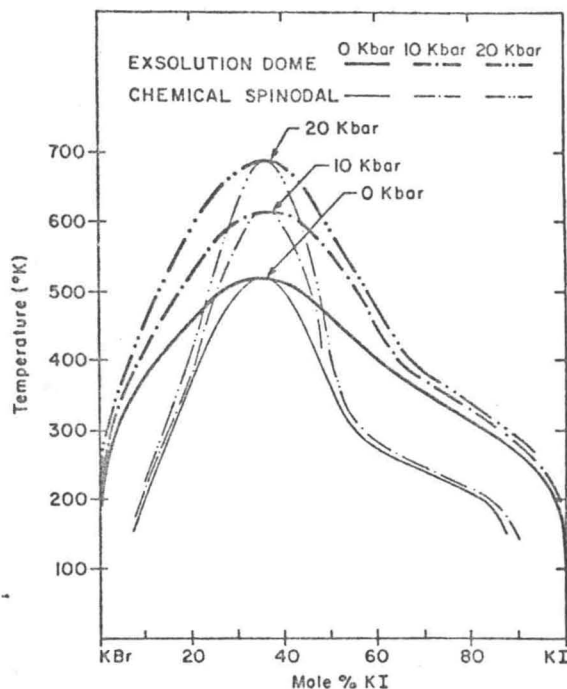


Fig. 3. Exsolution dome and chemical spinodal of KBr-KI for three pressures.

temperature difference with pressure. The third factor $1/N_0$ is the volume per molecule and decreases monotonically with pressure.

The data of Table 3 indicate that for LiBr-LiI and for KBr-KI the maximum of the coherent spinodal should lie very close to 300°K, so that no spinodal decomposition is to be expected at room temperature. For NaBr-NaI, RbBr-RbI and NaCl-KCl, however, the maximum of the coherent spinodal lies from 50° to 100°C above room temperature, and spinodal decomposition should take place. This is contrary to the observations of Wolfson *et al.*[14], who did not observe spinodal decomposition in NaCl-KCl at room temperature. Probably this discrepancy reflects the large uncertainty of the theoretical estimates for the coherent spinodal.

In spite of the uncertainty in the absolute magnitude of T_{coh} one should expect the pressure dependence to be predicted correctly. Thus spinodal decomposition may be ex-

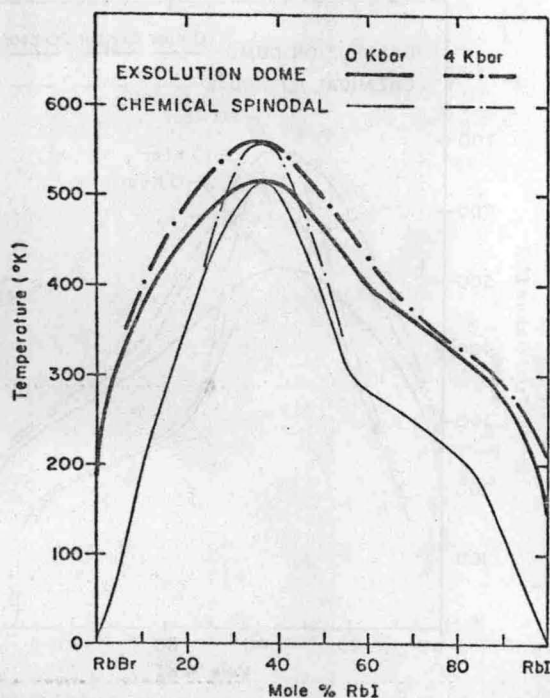


Fig. 4. Exsolution dome and chemical spinodal of RbBr-RbI for two pressures.

pected to occur at high pressure for LiBr-LiI, KBr-KI, and KCl-NaCl, whereas in NaBr-NaI very high pressure (above 50 kbar) should suppress spinodal decomposition if it were ever favored at intermediate pressures. For RbBr-RbI spinodal decomposition may take place at pressures close to the phase transition at 4 kbar, but the rise of T_{coh} is not large enough to predict this effect with certainty.

It is interesting to note that for LiBr-LiI, NaBr-NaI and NaCl-KCl the elastic anisotropy factor α changes sign at pressures of the order of 45, 35 and 8 kbar, respectively. One may therefore conclude that for these systems the direction of spinodal decomposition should change from $\langle 100 \rangle$ at low pressures to $\langle 111 \rangle$ at high pressures, whereas for the remaining systems KBr-KI and RbBr-RbI decomposition should occur in $\langle 111 \rangle$ at all pressures.

For the system NaCl-KCl the spinodal curves have not been included in Fig. 5 since

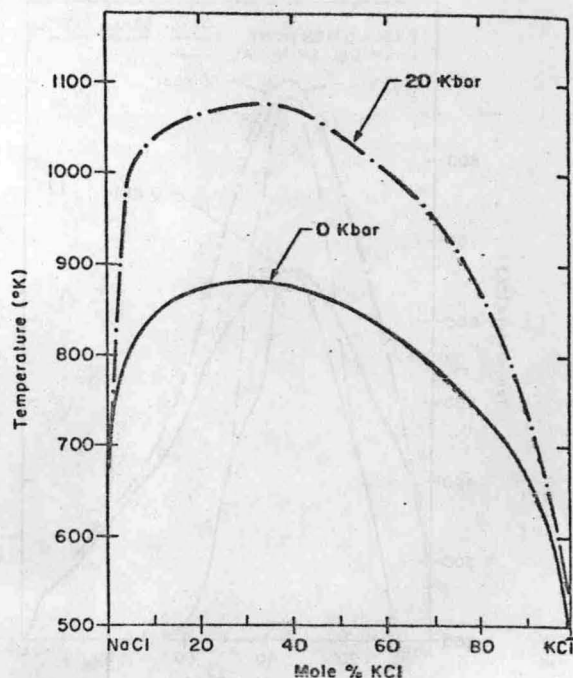


Fig. 5. Solid solubility curves for NaCl-KCl at two different pressures.

for this system the free energy-vs. composition curve shows three minima, instead of the usual two. The exsolution dome shown in Fig. 5 was obtained from the common tangent to the two minima corresponding to the lowest and highest compositions, respectively.

The occurrence of three minima in the free energy curve would be indicative of an ordered phase resulting in two exsolution domes and two spinodal curves. No such effect has been observed, however, in alkali halides. In two papers, which only recently came to our attention, Hovi[41,42] reports theoretical results for KBr-KI and RbBr-RbI solid solutions which show the same effect. These results are based on the theory of Wasastjerna [43, 44] which includes the entropy contribution from local order but does not include the vibrational entropy contribution. Since for the theoretical model used in the present work only one solubility gap is obtained for KBr-KI and RbBr-RbI it is suggested that the occurrence of two solubility gaps arises from the entropy term, and not from the heat of formation. The results obtained for these two systems and, on the basis of the present model, for NaCl-KCl seem to indicate that both the entropy contribution from local order and the vibrational entropy can cause two solubility gaps. Since experimental verification of two solubility gaps would be a rather difficult task the question must remain undecided whether the theoretical entropy contributions due to local order

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

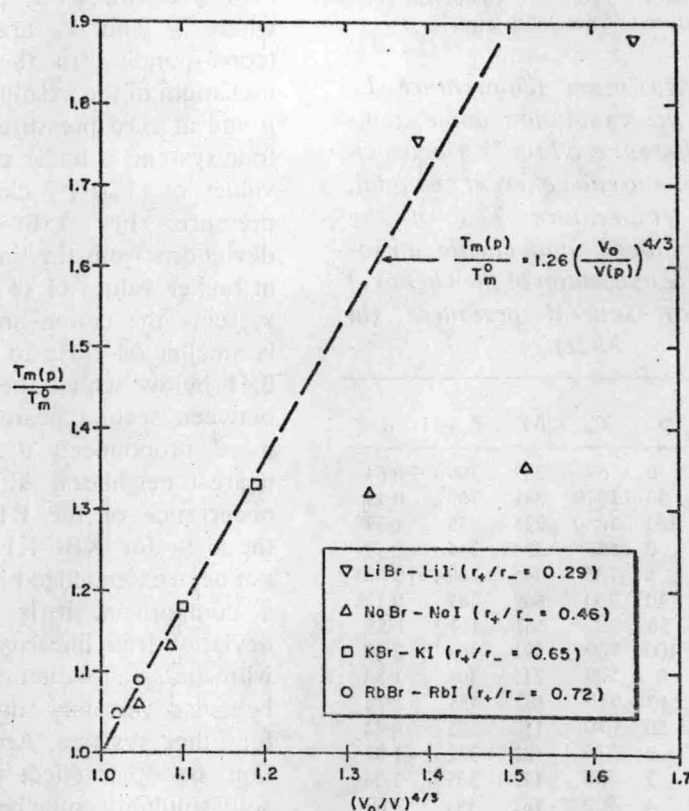


Fig. 6. Dependence of maximum temperature of exsolution dome on volume for several pressures and several systems.

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

with increasing pressure. It would be interesting, although quite difficult, to verify this effect experimentally.

In order to check the theoretical results it would be desirable to have experimental data on solid solubility as a function of pressure. Such measurements for the system NaCl-KCl have been performed in this laboratory[33] and are in reasonable agreement with the theoretical data. However, no spinodal decomposition has been observed. Another possible experiment would be the investigation of the system KBr-KI in the pressure range 0-20 kbars. By application of a rapid quench technique in order to reach the unstable region under the exsolution dome, unambiguous experimental verification of spinodal decomposition in alkali halides might be obtained.

Acknowledgement—The authors would like to thank Professor R. Roy for his interest in this work, for many stimulating discussions, and for a preprint of his paper prior to publication.

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LATTICE THEORY OF ALKALI HALIDE SOLID SOLUTIONS—III.
PRESSURE DEPENDENCE OF SOLID SOLUBILITY AND SPINODAL
DECOMPOSITION

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Erratum:

Ref. 33 should read: M.C. Bhardwaj and R. Roy, *J. Phys. Chem. Sol.* 32, 1603 (1970).