

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

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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-