

## Solid solutions of alkali halide compounds: A new model

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(Received 21 July 1986)

A new model is presented for calculating the thermodynamic properties of concentrated alloys of alkali halide compounds using ion-ion potentials. The model determines the mean pair-interaction energy and the mean near-neighbor separation by performing an average on end-member pair potentials over the ground state of the alloy at a given concentration. By using these, an ion-ion potential is constructed to describe the interaction between "pseudoions" situated on a lattice. The free energy and its derivatives for the lattice of "pseudoions" are calculated using an average quasiharmonic approximation. When applied to  $\text{KCl}_{1-x}\text{NaCl}_x$  ( $0 \leq x \leq 1$ ) alloy, the model successfully demonstrates its potential to yield quantitative results.

Approximate schemes to obtain the thermodynamic properties of concentrated alloys provide a convenient framework for an understanding of these systems. Well-established procedures exist to obtain, for instance, the phase diagram in the case of metallic alloys.<sup>1</sup> Usually, the configurational free energy of an alloy is computed at constant volume neglecting the vibrational free energy. This approximation works very well for metals.<sup>1</sup> Alloys of alkali halides, however, differ from metallic alloys in that the change in volume, upon alloying, has considerable influence on the thermodynamic behavior. That is, a constant pressure calculation allowing for the volume change and accounting for the vibrational free energy has to be performed.

It is shown here that a systematic scheme can be formulated to include the volume effect and the vibrational contribution in the determination of the free energy of disordered alkali halide alloys.

It is assumed in the model that, for the calculation of thermodynamic properties of an alloy at a given concentration  $x$ , (i) the interactions in the ground state of the al-

loy can be described by suitably constructed average ion-ion interaction potentials, (ii) an average volume can be defined for the ground state taking into account the distribution of equilibrium separations between the ions, and (iii) the details of the vibrational spectrum are not important permitting sums over phonon frequencies to be replaced by an average frequency.

The first two assumptions define the alloy as consisting of "pseudoions" situated on a regular lattice, as will be seen below. The last assumption is used to calculate also the free energies of the end members. That (i) and (ii) are related can be seen through the use of effective pair potentials to describe the interactions in the alloy.

In what follows, we shall illustrate the model for near-neighbor (NN) interactions with an additional assumption that (iv) the ground state of the alloy is completely disordered. The systems considered are those whose end members have one ion in common and belong to NaCl-type crystal structure, (e.g.,  $\text{KCl}_{1-x}\text{-NaCl}_x$ ). These systems display many essential features of concentrated alloys of alkali halides.

TABLE I. The input to determine end-member NN interionic potentials. The calculated potential parameters and the lattice parameters at 300 K are also given along with room-temperature data taken from Ref. 2. (The lattice parameters at 0 K were obtained from room-temperature values using thermal expansion coefficient data in Ref. 8.)

	KCl	NaCl
Cohesive energy at 0 K (ergs)	$-1.1104 \times 10^{-11}$	$-1.2406 \times 10^{-11}$
Lattice parameter at 0 K (Å)	3.113	2.79
Calculated potential parameters		
$A$ (ergs)	$3.7323 \times 10^{-10}$	$4.4760 \times 10^{-10}$
$\alpha$ (Å <sup>-1</sup> )	2.2914	2.5884
Calculated lattice parameter at 300 K (Å)	3.1456	2.8135
Room-temperature lattice parameter (Å)	3.147	2.82

The NN ion-ion potential in pure alkali halides is well represented by the functional form<sup>2</sup>

$$u(R) = \frac{-\alpha_M e^2}{R} + 6Ae^{-\alpha R}, \quad (1)$$

where  $R \equiv |\mathbf{R}|$ ,  $\alpha_M$  is the Madelung constant, and  $e$  is the electronic charge. We determine the repulsive parameters  $A$  and  $\alpha$  of end members using the experimental cohesive energy [van der Waals contributions are subtracted; zero-point energy is included within the average quasiharmonic approximation (1f-AQH)] and the experimental NN separation at  $T=0$  K (see Table I). The potential can describe the interactions close to and including a regular configuration. In the ground state of the alloy each ion reacts to several environments due to many-body interactions and will therefore have a distribution of equilibrium separations from its neighbors. That is, even though the near neighbors in the alloy are essentially the same as in the corresponding end members, the nature of interactions is not. We incorporate this feature, approximately as follows. The  $n$ th environment is defined as containing  $n$  substitutional defects and  $6-n$  host ions (coordination number  $z=6$  for NaCl-type structure) situated at an equilibrium separation  $R_n^{(0)}$  from the common ion.  $R_n^{(0)}$  is determined by demanding that the interaction energy of this environment,  $u^{(n)}(R_n)$ , satisfy the equilibrium condition:

$$u^{(n)}(R_n) = \frac{-\alpha_M e^2}{R_n} + V^{(n)}(R_n) \quad n=0,1,\dots,6. \quad (2)$$

The second term is the total short interaction energy per pair written as

$$V^{(n)}(R_n) = (6-n)V_1(R_n) + nV_2(R_n), \quad 1,2: \text{ end members}, \quad (3)$$

where

$$V_i(R_n) = V_i(R_i) + (R_n - R_i) \nabla V_i |_{R_i} + \frac{1}{2} (R_n - R_i)^2 \nabla^2 V_i |_{R_i} + \dots, \quad i=1,2 \quad (4)$$

terms beyond second order in the Taylor expansion are neglected; i.e., in each environment, the deviation from the end-member equilibrium separation is taken to be small. The equilibrium condition  $(du^{(n)}/dR_n)|_{R_n^{(0)}}=0$  gives

$$\begin{aligned} \frac{\alpha_M e^2}{(R_n^{(0)})^2} + R_n^{(0)} [(6-n) \nabla^2 V_1(R_1) + n \nabla^2 V_2(R_2)] \\ = (6-n) [R_1 \nabla^2 V_1(R_1) - \nabla V_1(R_1)] \\ + n [R_2 \nabla^2 V_2(R_2) - \nabla V_2(R_2)]. \quad (5) \end{aligned}$$

$R_n^{(0)}$  is determined iteratively. If  $p_n(x)$  is the probability of the occurrence of the  $n$ th environment at concentration  $x$ , the average interaction energy and NN separation over all environments is

$$\bar{u}(\bar{R}) = \langle u^{(n)}(R_n^{(0)}) \rangle = \sum_n p_n(x) u^{(n)}(R_n^{(0)}), \quad (6a)$$

$$\bar{R} = \langle R_n^{(0)} \rangle = \sum_n p_n(x) R_n^{(0)} \quad (6b)$$

for complete disorder,  $p_n(x) = 6C_n(1-x)^{6-n}x^n$ . Here it is assumed that all arrangements of  $n$  defects and  $6-n$  host ions are equivalent.

To construct the ion-ion potential for the alloy, we write  $\bar{u}(\bar{R})$  in the form given in Eq. (1). Knowing  $\bar{u}(\bar{R})$  and  $\bar{R}$  and using the equilibrium condition, one can determine  $\bar{A}$  and  $\bar{\alpha}$  (bar denotes that they are composition-dependent average potential parameters). This potential describes interactions between "pseudoions" in configurations close to and including the regular lattice.

The use of the Madelung constant in Eq. (2) implies that the Coulomb-interaction energy of each ion with all the other ions in the entire system is defined by the NN spacing with respect to this ion. This is an approximation. However, it can be seen that

$$\left\langle \frac{-\alpha_M e^2}{R_n^{(0)}} \right\rangle = \frac{-\alpha_M e^2}{\langle R_n^{(0)} \rangle}, \quad (7)$$

and the Madelung energy appearing in Eq. (6a) is valid on the average. Having determined the ion-ion potentials, the Hamiltonian can be written down as

$$H = \sum_{N,\nu,i} \frac{p_i^2(N,\nu)}{2m_\nu} + \frac{1}{2} \sum_{\substack{\nu,\pi, \\ N,P}} v_{\nu\pi}(r(N,\nu;P,\pi)), \quad (8)$$

where  $N$  and  $P$  are unit-cell indices,  $\nu$  and  $\pi$  are indices labeling the type of ion in the unit cell,  $m_\nu$  is the mass of an ion of type  $\nu$ , and  $i=x,y,z$  labels Cartesian coordinates;  $p_i(N,\nu)$  is the  $i$ th component of the momentum of the  $\nu$ th ion in the  $N$ th unit cell and  $v_{\nu\pi}(r(N,\nu;P,\pi))$  is the potential energy of interaction between ions  $N\nu$  and  $P\pi$ , which are separated by  $r$

$$r(N,\nu;P,\pi) = \mathbf{R}(N,\nu) - \mathbf{R}(P,\pi) + \boldsymbol{\eta}(N,\nu) - \boldsymbol{\eta}(P,\pi).$$

Here,  $\mathbf{R}$  describes the equilibrium position of an ion, while  $\boldsymbol{\eta}$  is its dynamical displacement. The approach to obtain the average quasiharmonic approximation is given by Shukla *et al.*<sup>3</sup> For a diatomic crystal there are  $6N_0$  vibrational modes labeled by the wave vector  $\mathbf{k}$  and branch index  $\lambda$ . In 1f-AQH a single frequency is obtained by averaging over all these modes:

$$\langle \omega^2 \rangle \equiv (6N_0)^{-1} \sum_{k,\lambda} \omega_{k\lambda}^2, \quad k \equiv |\mathbf{k}|$$

within 1f-AQH,

$$\omega \simeq \langle \omega^2 \rangle^{1/2} \quad \text{with} \quad \langle \omega^2 \rangle = \nabla^2 v_{\text{NC}},$$

where  $v_{\text{NC}}$  is the non-Coulombic potential. Explicitly,

$$\langle \omega^2 \rangle \simeq \omega^2 = \frac{\alpha}{\mu} A e^{-\alpha R} \left[ \alpha - \frac{2}{R} \right],$$

where  $\mu^{-1}$  is the reduced mass

$$F = N_0 \left[ \frac{-\alpha_M e^2}{R} + 6Ae^{-\alpha R} + 6k_B T \ln \left[ 2 \sinh \left( \frac{1}{2} \beta \hbar \omega \right) \right] \right], \quad \beta = (k_B T)^{-1},$$

$F$  is the total free energy,  $N_0$  is the Avogadro number,  $k_B$  the Boltzmann constant, and  $\hbar$  the Planck's constant di-

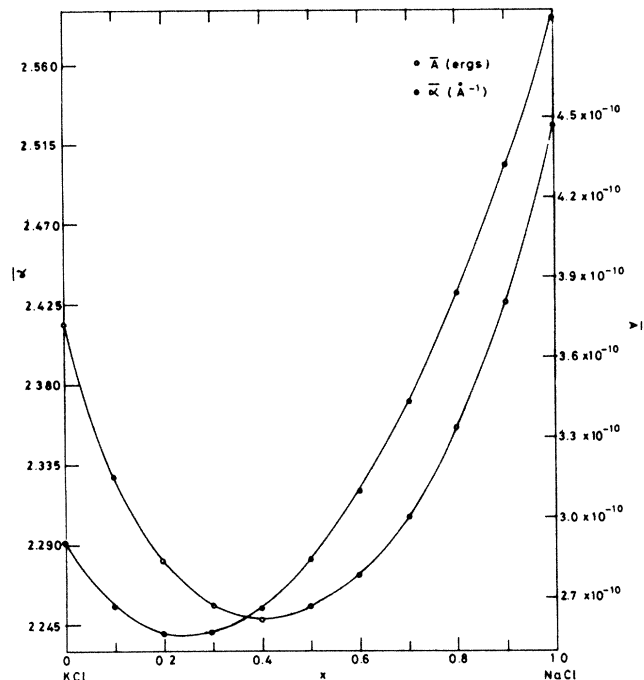


FIG. 1. Composition-dependent average ion-ion potential parameters. Determination required six-digit accuracy.

vided by  $2\pi$ .  $F$  must satisfy the relation  $P = -(\partial F/\partial V)_T$  ( $P$  the external pressure).  $P=0$  in our calculations. For the alloy, the configuration entropy is, for complete disorder,

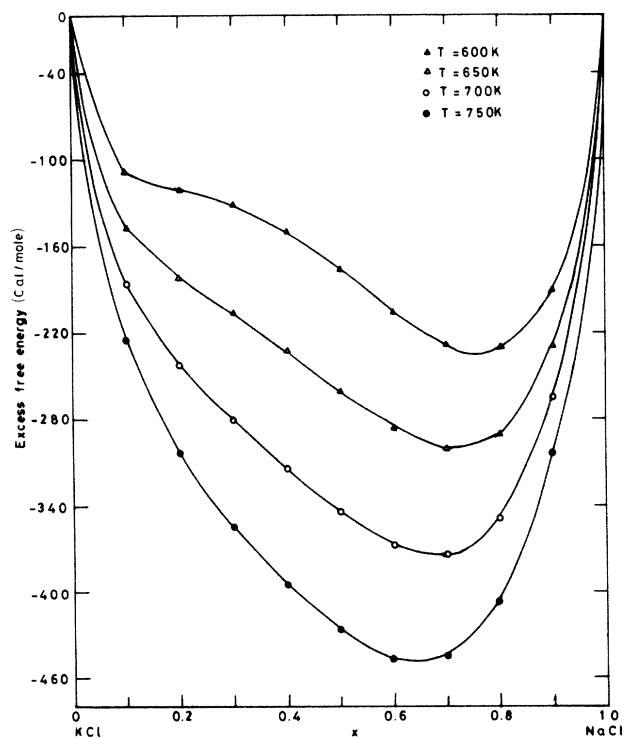


FIG. 2. Excess free energy ( $\Delta F$ ) at various temperatures. For  $T \geq 700$  K, the alloy is in solid solution over the entire composition range.

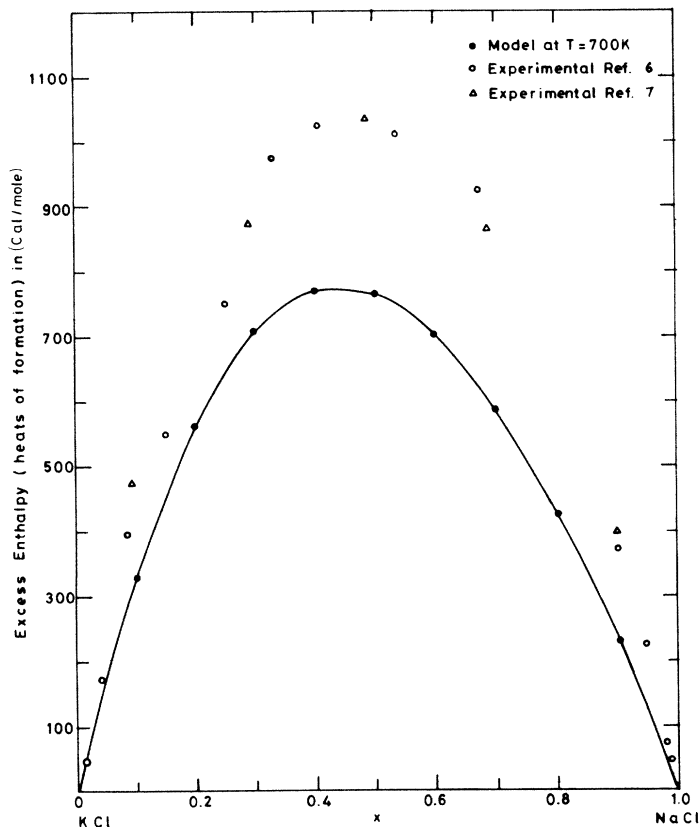


FIG. 3. Excess enthalpy ( $\Delta H$ ) calculated at 700 K and zero pressure. Measurements performed at 298 K and atmospheric pressure on a sample frozen in from 900 K.

$$S_{\text{config}} = k_B [(1-x)\ln(1-x) + x \ln x]$$

and the reduced mass is

$$\mu_{\text{alloy}}^{-1} = (1-x)\mu_1^{-1} + x\mu_2^{-1}, \quad 1,2: \text{ end members.}$$

We choose  $\text{KCl}_{1-x}\text{NaCl}_x$  to test the model. This system is one of the high-temperature alloys ( $T_c \sim 773$  K) (Ref. 4) in the alkali halide family and the volume difference between the end members at room temperature is close to the limits of solubility.<sup>5</sup> The results are contained in Figs. 1–4 along with the experimental data. The locus of the points defined by  $(\partial \Delta F/\partial x)=0$  yields the phase separation curve in the  $x$ - $T$  plane. The present scheme attempts to describe the alloy in equilibrium by determining the phase separation curve approximately. In Fig. 2, the convex portions of the excess free energy as a function of  $x$ , at a given temperature, indicate that the alloy is metastable or unstable for the corresponding values of  $x$ . It is seen that at  $T \geq 700$  K the excess-free-energy curve begins to develop a single minimum between  $x=0.6$  and  $x=0.7$ . The temperature ( $T_c$ ) and concentration ( $x_c$ ) at which a single minimum appears indicate the critical point for the alloy. From experiment,<sup>4</sup>  $T_c \sim 773$  K and  $x_c = 0.69$ . For  $T > T_c$ , the alloy is in thermodynamic equilibrium at all compositions. Accordingly, the excess enthalpy is ob-

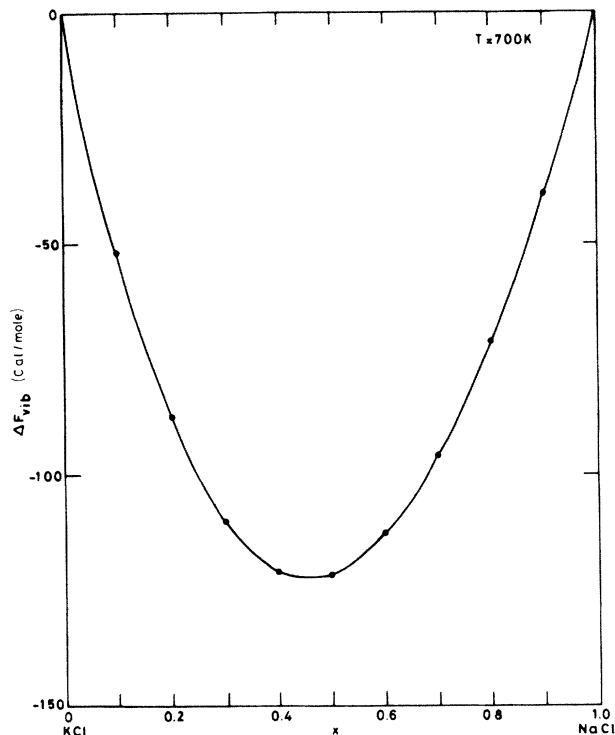


FIG. 4. Excess vibrational free energy ( $\Delta F_{\text{vib}}$ ) calculated at 700 K.

tained at 700 K (Fig. 3), close to  $T_c$  determined from the model. Available experimental data have been taken at room temperature on a sample frozen from  $T \geq 900$  K.<sup>6,7</sup> The sample frozen from  $T \approx 773$  K yielded  $\sim 15$  cal/mole

less.<sup>7</sup> The calculated  $\Delta H$  differs from experiment by a factor of 0.4. It may be noted that the present calculation is at zero pressure while the experimental results pertain to atmospheric pressure. The effect on  $\Delta H$  due to this pressure difference could be significant. It is found that the vibrational contribution to  $\Delta H$  ( $\Delta H_{\text{vib}}$ ) is negative and accounts for about  $\sim 12\%$  of  $\Delta H$ . The excess vibrational entropy  $\Delta S_{\text{vib}}$  has been determined and is 10% of  $\Delta S_{\text{config}}$ . From Fig. 4, we see that the excess vibrational free energy ( $\Delta F_{\text{vib}}$ ) contributes nearly 35% to the total excess free energy. Furthermore, the composition dependence of  $\Delta F_{\text{vib}}$  and  $\Delta H_{\text{vib}}$  influences the shape of the excess-free-energy curve at a given  $T$ , thus affecting the determination of the phase separation curve. In Fig. 1, the composition dependence of  $\bar{\alpha}$  and  $\bar{A}$  is shown. The behavior reflects the many-body effects implicit in the functional form given in Eq. (1). ( $\bar{\alpha}$  and  $\bar{A}$  are also correlated for the same reason.) From the present calculation, it is clear that for the systems under consideration the vibrational contribution to enthalpy and free energy are important. Earlier estimates<sup>5</sup> of  $\Delta H$ , neglecting thermal contributions, were close to or higher than the experimental values.

It is to be noted that the required quantities of end members and the alloy are calculated within 1*f*-AQH. The advantages of the present scheme are that (i) it is based on ion-ion potential determined completely by the end-member potentials, (ii) the vibrational entropy as well as configurational entropy is taken into account, and (iii) the model can be improved, systematically enabling the calculation of other point-defect related properties. Further work on the model is in progress and we hope to present the results in the near future.

<sup>1</sup>D. de Fontaine, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1979), Vol. 34.

<sup>2</sup>M. P. Tosi, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1964), Vol. 16.

<sup>3</sup>K. Shukla *et al.*, *J. Phys. Chem. Solids* **46**, 83 (1985).

<sup>4</sup>N. B. Chanh, *J. Chim. Phys.* **61**, 1428 (1964).

<sup>5</sup>References to earlier work are collected in V. HariBabu and U. V. SubbaRao, *Prog. Cryst. Growth Charact.* **8**, 189 (1984); see

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<sup>7</sup>W. T. Barret and W. E. Wallace, *J. Am. Chem. Soc.* **76**, 366 (1954).

<sup>8</sup>D. C. Wallace, *Thermodynamics of Crystals* (Wiley, New York, 1972).