

Solid solutions of alkali halide compounds. I. Configurational and vibrational contributions

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We present a model to do quantitative thermodynamics of pseudobinary ionic solid solutions of the type $A_{1-x}B_xC$ ($0 \leq x \leq 1$). The model enables us to compute the phase diagram as well as certain physical properties of interest, starting from interionic potentials. The model is demonstrated with three systems: $K_{1-x}Rb_xI$, $KCl_{1-x}Br_x$, and $Na_{1-x}K_xCl$. The model incorporates the essential features of pseudobinary ionic solid solutions, namely, (a) the interdependence of volume and energy, (b) the presence of nonrandom distribution of the two species and associated configurational entropy, and (c) the vibrational contributions to the free energy and its derivatives. In this work, we make use of the single-frequency average quasiharmonic approximation to assess the vibrational corrections to the entropy and the phase diagram.

I. INTRODUCTION

We study the equilibrium properties of essentially two component solid solutions. In particular, our primary interest is to model ionic solid solutions from interionic potentials and to address the question of how in a consistent manner vibrational contributions can be incorporated explicitly. The motivation has been to obtain the phase diagram and equilibrium physical properties within a single framework. Though models for specific properties are needed to highlight the issues involved, a single framework combining phase diagram determination with calculation of physical properties would be of fundamental interest. And a good starting point to model solid solutions would be from atomic interactions.¹

Specifically we choose solid solutions in the family of alkali halides, which crystallize in the NaCl-type structure, as representative of fully ionic systems for the demonstration of the model. The family of systems covers the essential features of a binary solid solution, namely, partial to complete solubility at high temperatures, asymmetry in the phase diagram, and physical properties with composition.^{2,3} Three systems are chosen in the present study to bring out the features of our model— $Na_{1-x}K_xCl$, $KCl_{1-x}Br_x$, $K_{1-x}Rb_xI$.

II. REVIEW

The basic features of the phase diagram have been obtained through a class of models^{4,5} based on the following assumption (these models originated from the mean-field theoretic treatment of the Ising model): the total partition function for the solid solution is factored into configurational and vibrational parts,

$$Z = Z_{\text{config}} Z_{\text{vib}} .$$

The two parts are handled independently.

A. Configurational entropy

Z_{config} is written in terms of appropriate configurational variables and is minimized with respect to them⁴

using either of the two well-known combinatorial methods: the quasichemical approximation^{6,7} (QCA) or the cluster variation method (CVM).^{4,8(a),8(b)} These methods were developed mainly to obtain better approximations to the configurational entropy.⁴ And to this extent, bond energies are treated as adjustable parameters. Such an approach can at best serve to verify the correctness of the combinatorial procedures, for there is no way to obtain any other property of the solid solution. Nevertheless, schemes that make use of QCA or CVM are preferable since the often-made assumption of random distribution of species leads to an overestimate of the configurational entropy. This would mask other contributions when comparison with experiment is made.

B. Configuration energy

As we go from metallic solid solutions to the other extreme, namely, ionic solid solutions, the bond energies will depend very much on the bond lengths and methods to obtain bond energies explicitly must be sought. We shall briefly review here the key concepts of existing models for handling configurational energy relevant for solid solutions of nonmetals.

There are two approaches to account for relaxations.

(a) To allow for relaxations locally with respect to a mean lattice spacing. The change in the energy due to the local strain δ is of the form

$$E = C\delta^2 ,$$

where $\delta = (R_{\text{imp}} - \bar{R}_{\text{host}})$ with R_{imp} as the impurity-host bond length and \bar{R}_{host} as the mean lattice spacing of the host.⁹ The form for C is fixed from single impurity calculations. Alkali halides of type $KCl_{1-x}Br_x$ (Refs. 10–12) and semiconductors of type $A_{1-x}B_xC$ (Refs. 13–15) have been treated in this manner.

(b) To minimize the energy of the unit cell, local relaxations inclusive, for specific relative arrangements of the two species.^{16–18} These methods give reasonable values for the heats of formation. Such methods, however, can-

not be used for determining energy derivatives with which we are concerned (we need volume derivatives of energy for equation of state calculations).

C. Vibrational entropy

Taking only the vibrational entropy (s_{vib}) to contribute to the Gibbs free energy (g) we can write the excess Gibbs free energy (Δg) for the solid solution as

$$\Delta g = \Delta g_{\text{config}} - T\Delta s_{\text{vib}} ,$$

where T is the temperature. It is clear that a positive value for Δs_{vib} can lead to a lowering of the critical temperature for phase separation. From the well-known high-temperature limit of the vibrational entropy in the Einstein model¹⁹ for a monatomic solid, expressed per mole,

$$s \simeq 3k_B [1 - \ln(\beta \hbar \omega_E)] ,$$

where $\beta = 1/k_B T$, ω_E is the effective single frequency, the standard expression for the excess vibrational entropy of a solid solution is given as

$$\Delta s_{\text{vib}}(x) = 3k_B \ln(\omega_1^{1-x} \omega_2^x / \omega_{\text{SS}}) ,$$

where $\omega_{1,2}$ and ω_{SS} are the effective frequencies of the end members and the solid solution, respectively.

The expressions can be rewritten in terms of the Debye temperatures and contact with experiment can be made since it is possible to deduce Debye temperatures from elastic-constant data, specific-heat data, etc., on solid solutions.^{2,20,21} In particular, estimates from x-ray-diffraction data suggest a positive excess vibrational entropy.²²

Fancher and Barsch¹⁰ have obtained, using elastic-constant data on solid solutions, a significant lowering of the coexistence curve for alkali halide solid solutions.

Lattice dynamical calculations on model solid solutions have been performed, mostly in the virtual-crystal approximation (VCA), to study the compositional dependence of the observable part of the vibrational spectrum.²³ For instance, for a system like $A_{1-x}B_xC$ Varshney *et al.*²⁴ evaluate the behavior of the phonon spectrum assuming the average force constant f to be of the form

$$f(x) = (1-x)f_{AC} + xf_{BC} .$$

By treating the degree of order as a perturbation on a virtual crystal, Kirkwood^{25(a)} has shown that inclusion of atomic vibrations lowers the critical temperature for the order-disorder transition.²⁶

III. PRESENT APPROACH

Only isostructural, homogeneous single phase regions of the phase diagram will be considered for equation of state (EOS) calculations. Given the experimentally observed crystal structure, the enumeration of the system's energy levels at overall composition x and temperature T can be made tractable by making the following observation.

Experimental time scales determine the most probable configuration and are longer than atomic diffusional time scales which in turn are longer than lattice vibrational time scales. That is, the arrangement of A and B atoms, at a given overall composition x , changes with temperature and since the vibrational states of the system depend on the atomic arrangement, a Hamiltonian that is a function only of x will be inadequate.

The general procedure for the given structure would then be as follows: at x , generate possible configurations; express the Gibbs free energy in terms of configuration variables; and determine the most probable configuration by minimizing the free energy with respect to configurational variables at (x, T) . This would mean each possible configuration is to be considered as a trial "ground state" with a corresponding Hamiltonian. The temperature dependence of the solid solution, at x , is obtained by forming a set of "ground states" each of which gives the minimum free energy at each temperature. And the temperature dependence of various physical properties will be nontrivial since at each temperature we have distinct configurations to evaluate from.

We shall take $\text{Na}_{1-x}\text{K}_x\text{Cl}$ as a typical system in what follows. It is a diatomic lattice of NaCl type with $z=6$ as the coordination number. The dominant interactions are the long-range Coulomb part which is dependent only on positional disorder and the nearest-neighbor (NN) short-range repulsive part which depends on local composition as well. We introduce cluster variables as configurational variables and choose the z NN sites around a common anion site as our basic cluster. The composition of the cluster is indexed by n , the number of K^+ ions among the z possible sites. Thus a cluster with $n=2$ will have four Na^+ ions and two K^+ ions with respect to a Cl^- ion. There are $z+1$ distinct cluster types if we assume that all the ways of arranging n K^+ ions among z sites are energetically equivalent. A configuration is defined by the set of occurrence probabilities $\{p_n\}$ of clusters of each kind (for convenience we shall refer to $\{p_n\}$ as $[p]$ from now on). $W([p])$ denotes the number of ways of arranging the clusters and the total energy of the configuration is assumed to be independent of the different arrangements of the clusters. In view of the nature of the interactions considered, this is a reasonable assumption. If $H([p])$ denotes the Hamiltonian for a configuration $[p]$, the partition function Z can be written down as

$$Z = \sum_{[p]} W([p]) \sum \exp\{-\beta H([p])\}, \quad \beta = 1/k_B T .$$

The second sum is over all the vibrational energy levels for a given $H([p])$. The Hamiltonian is taken to be the same for all the W ways of constructing the configuration $[p]$.

Formally, the most probable configuration is given by the condition

$$\partial \ln Z([p]) / \partial [p] = 0 .$$

We note that while $W([p])$ can be an explicit function of $[p]$, it is quite difficult to express the second sum in closed form as an explicit function of $[p]$ due to the presence of compositional and positional disorder.^{25(b)}

We first assume that the most probable configuration is determined using the configurational partition function. And for this configuration, vibrational contributions as well as all the thermodynamic quantities of interest are to be evaluated. This assumption leads to replacing Z by Z_{config} in the differentiation with respect to $[p]$,

$$\partial \ln Z_{\text{config}}([p]) / \partial [p] = 0 .$$

The most probable configuration will be denoted by $[\bar{p}]$. To minimize with respect to $[p]$ and to evaluate $W[\bar{p}]$ among other things we employ a suitably extended version of the quasichemical approximation (see Sec. V).

We next parametrize the solid solution using the properties of the configuration $[\bar{p}]$ (see Sec. VIII). The parameters can be said to define the interactions in the solid solution as that between pseudoions sitting on a regular lattice. Such a regular configuration is considered to be a suitable representation of the most probable configuration for the solid solution at x and T . Unlike in the virtual-crystal approximation where the atoms are arranged in a completely random manner on sites of a perfect lattice at constant volume, the present approxima-

tion allows us to follow the state of a typical solid solution in the (x, T) plane much more closely.

The Hamiltonian with these effective potentials being identical in form with that for the end members, subsequent procedures to evaluate the various thermodynamic quantities of interest from the EOS will be the same in both cases. Further, since the solid solution at x and T is treated on the same footing as end members, we expect the calculation of the solidus temperature to be feasible if the calculation of melting temperatures for end members is.²⁷

We then make the reasonable assumption that the calculation of EOS and thermodynamical quantities, for end members as well as for solid solutions, depends only on the averages over the phonon spectrum and hence can be evaluated using an effective single frequency.

Specifically, we make use of the single-frequency average quasiharmonic approximation²⁸ (1f-AQH) (see Appendix A).

A summary of the entire calculation sequence is given in Fig. 1 with notes in Appendix C.

IV. INTERACTION POTENTIALS FOR THE END MEMBERS

We consider the form in Eq. (1) in all the energy calculations, for the solid solutions as well as for end members: point charges on a NaCl-type lattice with NN repulsive potential (Born model, soft core). The lattice energy per ion pair is²⁹

$$\phi = -\alpha_M e^2 / R + z \mathcal{A} \exp(-\alpha R) . \quad (1)$$

α_M is the Madelung constant taken as 1.747 558 here; \mathcal{A} and α are short-range repulsive potential parameters; R is the NN lattice parameter.

However, to obtain α and \mathcal{A} for the end members we must apportion energy between various terms as correctly as possible and hence van der Waals (vdW) interaction terms are included for this purpose and the form below is used for the semiempirical determination of α, \mathcal{A} :

$$u = -\alpha_M e^2 / R + z \mathcal{A} \exp(-\alpha R) - C / R^6 - D / R^8 , \quad (1a)$$

where C and D are, respectively, dipole-dipole and dipole-quadrupole coefficients of the vdW interaction in-

TABLE I. The input to determine end-member NN interionic potentials and the calculated potential parameters α , at $T=300$ K. R is the lattice constant and B_T is the isothermal bulk modulus. Data taken from Ref. 29. Note: We have used Mayer's van der Waals interaction coefficients from the tabulation in Ref. 33.

Compound	R (Å)	B_T		
		(10^{11} dyn/cm ²)	α (Å ⁻¹)	(10^{-9} erg)
NaCl	2.82	2.4	3.187	2.539
KCl	3.147	1.74	3.101	4.649
KBr	3.298	1.48	2.997	5.074
KI	3.533	1.17	2.857	5.918
RbI	3.671	1.06	2.826	7.561

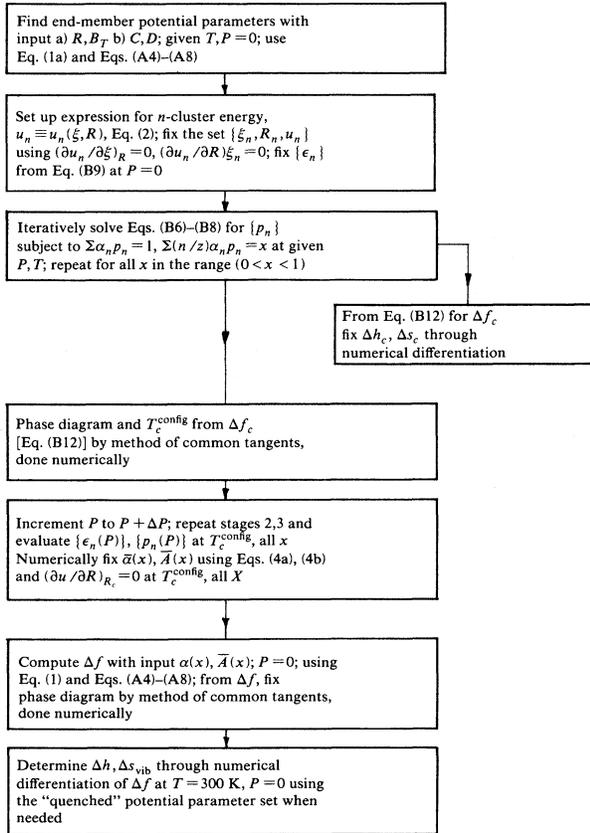


FIG. 1. We summarize here the computational sequence followed in the present work. Further details are given in Appendix C.

TABLE II. Properties of end members calculated, at $T=300$ K, from the potential parameters in Table I using $1f$ -AQH. Experimental values are given in parentheses. Entropy data are taken from Ref. 34, B_T values from Ref. 29, and all other data taken from Ref. 35.

Parameter	NaCl	KCl	KBr	KI	RbI
R (Å)	2.9282 (2.8203)	3.2739 (3.1467)	3.441 (3.299)	3.7018 (3.533)	3.8575 (3.671)
B_T (10^{11} dyn/cm ²)	2.0 (2.35)	1.391 (1.74)	1.152 (1.48)	0.8744 (1.17)	0.7613 (1.055)
C_{11} (10^{11} dyn/cm ²)	4.134 (4.87)	3.026 (4.064)	2.532 (3.463)	1.95 (2.71)	1.724 (2.573)
C_{12} (10^{11} dyn/cm ²)	0.9983 (1.311)	0.6268 (0.712)	0.5105 (0.581)	0.3763 (0.45)	0.3161 (0.3776)
ω_{AQH} (10^{13} Hz)	2.867	2.23	1.768	1.525	1.125
Infrared dispersion frequency (10^{13} Hz)	(3.078)	(2.667)	(2.14)	(1.917)	(1.408)
Entropy (kcal/mol,K)	16.48 (17.42)	19.78 (19.7)	22.74 (23.1)	24.8 (24.9)	28.7 (28.2)

clusive of structure constants.²⁹

The procedure to obtain α and \mathcal{A} within the $1f$ -AQH approximation is given in Appendix A. Results and the input experimental data used for the evaluation of α and \mathcal{A} for end members are given in Table I. In Table II we have presented the results of relevant properties, like ω_{AQH} and entropy, calculated from the potential parameters and the EOS, along with the corresponding experimental values for the three systems studied. We see from Table II that in spite of the various constraints on the functional form and the EOS, the calculated values bare a one-to-one correspondence with the values measured. It is encouraging to see a close agreement between experiment and model in the case of entropy.

V. ENERGIES OF N -CLUSTERS

In this section we detail the procedure used to determine the energies of n -clusters which forms the input for

TABLE III. Excess configurational entropy for the three systems at $T=300$ K along with the ideal mixing entropy.

x	ΔS_{config} (cal/mol,K)			ideal
	$\text{K}_{1-x}\text{Rb}_x\text{I}$	$\text{KCl}_{1-x}\text{Br}_x$	$\text{Na}_{1-x}\text{K}_x\text{Cl}$	
0.1	0.646	0.645	0.645	0.646
0.2	0.993	0.991	0.989	0.994
0.3	1.210	1.205	1.199	1.213
0.4	1.331	1.323	1.314	1.337
0.5	1.370	1.361	1.352	1.378
0.6	1.331	1.324	1.318	1.337
0.7	1.210	1.206	1.204	1.213
0.8	0.993	0.992	0.992	0.994
0.9	0.646	0.642	0.646	0.646

QCA (see Appendix B).

First, we tile n -clusters to form an infinite crystal in three dimensions.³⁰ We will have, for each value of n , a corresponding configuration [Fig. 2(a)]. The configurations are symmetric about $n=3$. These are termed reference compounds, as they provide an energy scale for the problem. And the important feature in this class is that every anion site has identical number n of K^+ ions [and $(z-n)$ Na^+ ions]. Next, we write down the energy of such configurations in a simple way—as energy per the corresponding unit cell. It has been possible to include ionic displacements and minimize the energy with respect to these displacements with the following assumptions.

(a) The displacement pattern is confined to the anion sublattice—with K^+ ions causing the NN Cl^- ions to move away along the line joining them because the $\text{K}^+ - \text{Cl}^-$ distance is larger than the $\text{Na}^+ - \text{Cl}^-$ distance.

(b) The electrostatic energy correction terms due to the ionic displacements are neglected.

The energy expression is just the weighted anion and cation site energies to give the total energy per unit cell—weighted to correct for double counting of sites and bonds. There are two sites, one cation and one anion site, per unit cell and the site energy is the total interaction energy of the ion at the site with the rest of the system. Explicitly, for $n=3$, we have

$$u_3(R, \xi) = -\alpha_M e^2 / R + v_3(R, \xi), \quad (2a)$$

$$v_3(R, \xi) = [2\mathcal{A}_2 \exp(-\alpha_2 R_1) + \mathcal{A}_2 \exp(-\alpha_2 R_+)] \\ + [2\mathcal{A}_1 \exp(-\alpha_1 R_1) + \mathcal{A}_1 \exp(-\alpha_1 R_-)], \quad (2b)$$

where $R_{\pm}^2 = (R \pm \xi)^2$; $R_1^2 = (R^2 + \xi^2)$; $R_2^2 = (R^2 + 2\xi^2)$. Similar expressions can be written down for $n=1,3$. Since the expressions are symmetric with respect to an interchange of Na^+ and K^+ ions, $n=4,5,6$ cases are also covered. The minimization conditions are

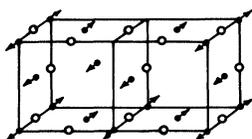
$$\{\partial v_n / \partial \xi\}_{\xi=\xi_n, R=0} = 0, \quad (3a)$$

$$\{\partial u_n / \partial R\}_{R=R_n, \xi=\xi_n} = 0. \quad (3b)$$

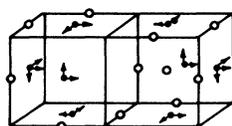
The values $\xi(R_n)$ and R_n are obtained iteratively from these conditions.

The numerical coefficients for repulsive interactions such as 1,2 in the above expressions are the result of considering bond and site double counting when writing down the energy of the configuration in terms of the energy of the unit cell. The reference compound defines the n -cluster energy uniquely, and is independent of x ($x \neq n/z$). We feel that the n -cluster energy in the corresponding reference compound can be regarded as the lowest energy state in analogy with $n=0$ and $n=z$ cases where it is so. These reference compounds are taken as purely hypothetical in nature for the present.¹⁸

$n = 3$

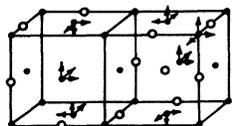


(a)



(b)

- - Larger of the two cations, here K^+
- - anions with directions of displacements indicated by arrows



(c)

FIG. 2. Two classes of configurations are illustrated here for a typical system like $\text{Na}_{1-x}\text{K}_x\text{Cl}$ at a given overall composition $x (= \frac{1}{2})$. (i) Composition that is maintained in each cluster through tiling. The resulting relaxation pattern is unique [see (a) and (c)], and (ii) composition that is maintained over an optimum sized "unit cell" leading to low-energy configurations [see (b)]. For clarity, the displacement pattern is restricted to a small number of ions. Site double counting and bond double counting are corrected for computing the energy of these unit cells. Note that the smaller cations are not shown in the figure.

VI. RESULTS

We see that the excess configurational free energy is determined completely by $[\bar{p}]$ which in turn is specified by $[\varepsilon]$. Since $[\varepsilon]$ is dependent on pressure P implicitly and since $[\bar{p}]$ is dependent on T , Δf_c is dependent on P, T . When $\varepsilon_n = 0$, all n , the set $[\bar{p}]$ goes over to $[p^*]$ as it should. Correspondingly, Δf_c reduces to Δf_{ideal} [see Eq. (B12)].

Values of ε_n are asymmetric about $n=3$ and the degree of asymmetry tends to increase with increasing disparity between the pair of end members which in turn leads to higher critical temperatures. Within QCA, systems differ from each other quantitatively through the magnitudes of the cluster energy set and qualitatively through the relative magnitudes within each set. Thus there exists a simple proportionality between T_c^{config} and the absolute magnitude of the cluster energy set. $\bar{p}_n(x)$ is fairly symmetry about $n=3$ and as a function of x peaks at $x \cong n/z$, all n for a given pressure and temperature. The occurrence of peaks at $x \cong n/z$ and the absence of any other structure in the composition dependence of $[\bar{p}]$ stems from the simple trend seen in the behavior of ε_n with respect to n . Moreover, for the same reason, we find no pronounced structure in the compositional dependence of other derived properties.

The crucial quantity in QCA is the configurational entropy Δs_c . We give in Table III the results for the three systems studied along with the ideal mixing entropy. The negative deviation from Δs_{ideal} is a common feature in all cluster based approximations, for systems for which $\varepsilon_n \geq 0$, all n . This negative deviation leads to $T_c^{\text{calc}} > T_c^{\text{expt}}$. However, since calculated excess enthalpy values turn out to be reasonably close to the experiment we have to seek other sources for bringing down T_c^{calc} , notably vibrational entropy.

VII. COMMENTS

We have sampled a few other configurations and computed cluster energies using the unit-cell procedure. Our results can be summarized as follows.

(a) Configurations with slightly larger unit cells but asymmetric with respect to interchange of Na^+ and K^+ ions [Fig. 2(b)] leads to a range of values of ε_n , both positive and negative.

(b) For $n=3$, a fully tiled energetically nonequivalent configuration could be constructed [Fig. 2(c)]. The excess cluster energy ε_3 in this case is surprisingly negative. From the expression for the cluster probability in terms of ε_n [Eq. (B9)], it is seen that a negative ε_3 can lead to $\bar{p}_3 > p_3^*$. And negative excess energies can lead to a structure in the phase diagram.^{14,18} However, since the existing experiments on the systems considered do not reveal any structure, we have not used this configuration for our calculation of $[\bar{p}]$.

(c) Configurations having ordered sublattices (fcc) (Ref. 18) lead to complete cancellations of displacements for all n with consequent high energies.

(d) Independent-cluster approximation: it is based on

the observation that in QCA, the most probable configuration is constructed from the knowledge of the cluster populations and not from the exact distribution of various clusters. Hence it may be thought that clusters can be uncoupled from the environment for the purposes of cluster energy calculation.¹⁴ In the present context, the absence of relaxational contributions from the immediate neighborhood leads to high cluster energies.¹⁷

The unit-cell procedure that we have introduced for the calculation of configurational energy, inclusive of relaxations, is based on the following picture.

At high concentrations of impurities we can consider the total displacement field to consist of a homogeneous part, which changes the mean volume of the whole system, and an inhomogeneous part, both of which contribute to the change in energy of the total system.³¹ We partition the system into equisized regions and introduce the set $\{\xi_i\}$ to describe the inhomogeneous displacement field in each region. If the clustering tendency among impurities is not pronounced, we expect, on the average, the same set of variables to describe the displacement field in every other region.³² Hence it is possible to write down

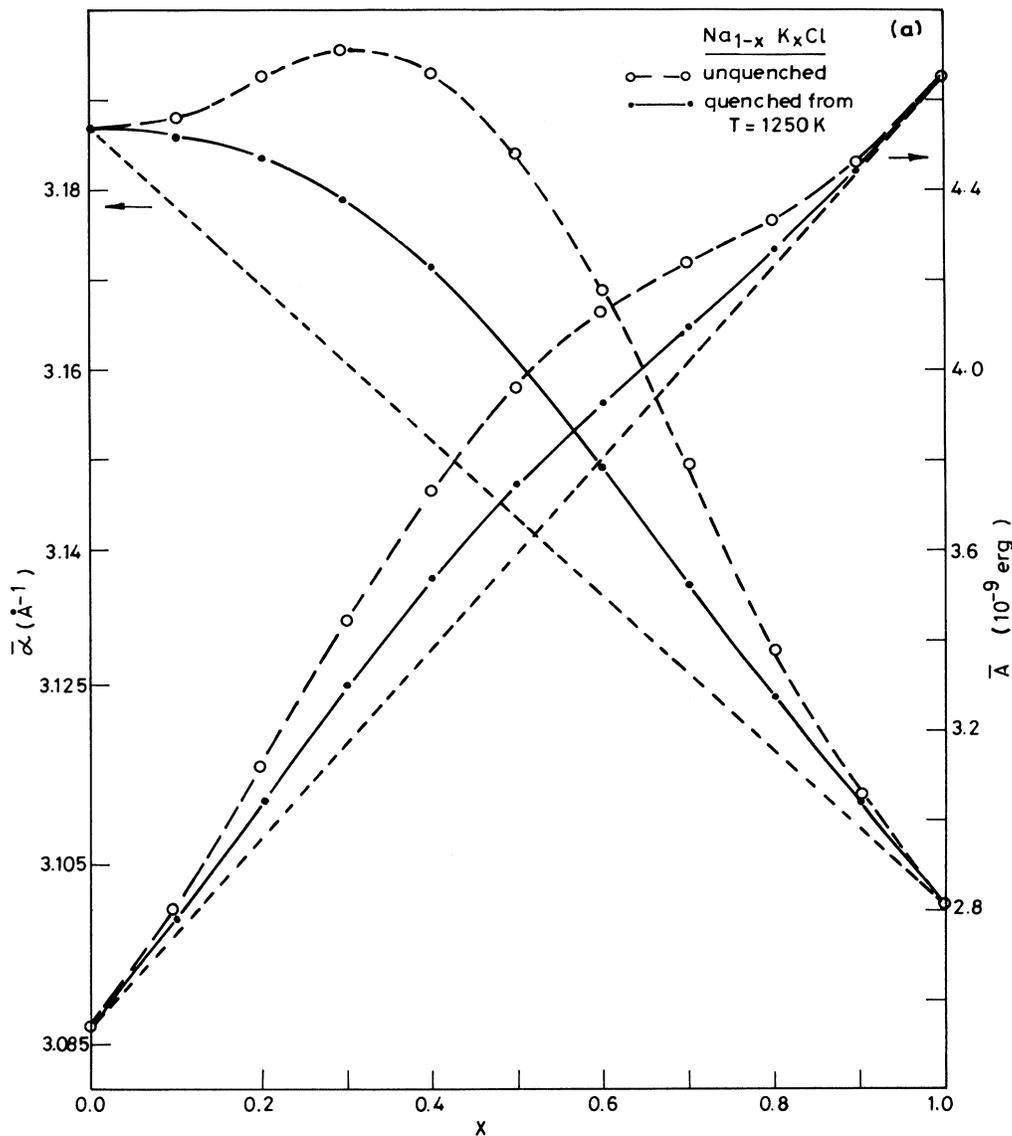


FIG. 3. Compositional dependence of the two effective potential parameters $\bar{\alpha}$ and \bar{A} , representing range and strength of the soft-core repulsive interactions (solid curve) in the solid solution. A linear dependence on composition is included for comparison (dashed line). In (a) the significance of the effect of "quenching" to 300 K from T_c is illustrated. The set of "quenched" parameters is used to describe a quenched sample. Even though \bar{A} increases over the mean, the increase in $\bar{\alpha}$ over the mean is such that there is an overall softening of the effective repulsive interactions.

the total energy of the configuration as a sum over energies of the regions (correcting for bond and site double count) in terms of the mean lattice parameter (treated as a free variable) and the set $\{\xi_i\}$ of displacement variables. Alternatively, we can perform a weighted sum over distinct site energies, weighted according to the frequency of occurrence of the corresponding sites. It follows that the "unit-cell" energy written as the weighted sum over distinct site energies gives the total configurational energy.

The displacement variables are arguments of the site energies, to be determined from minimization conditions. The mean volume of the system is obtained from the equilibrium condition applied to the variable R , the mean lattice parameter, which enters the argument of the site energy.

VIII. THE SOLID SOLUTION

We parametrize the solid solution using the configurational properties. For this it is convenient to work with $g_c[\bar{p}]$, the Gibbs free energy for the most probable configuration $[\bar{p}]$, and define enthalpy $h_c[\bar{p}]$ as

$$h_c = \frac{\partial(g_c/T)}{\partial(1/T)} = u = \alpha_M e^2/R + z\bar{A}e^{-\bar{a}R}, \quad (4a)$$

where we have equated it to the lattice energy per pair for NaCl-type crystal structure (u is the same as ϕ), and volume $v_c[\bar{p}]$ as

$$v_c = \{\partial g_c / \partial P\}_T = 2R_c^3; \quad (4b)$$

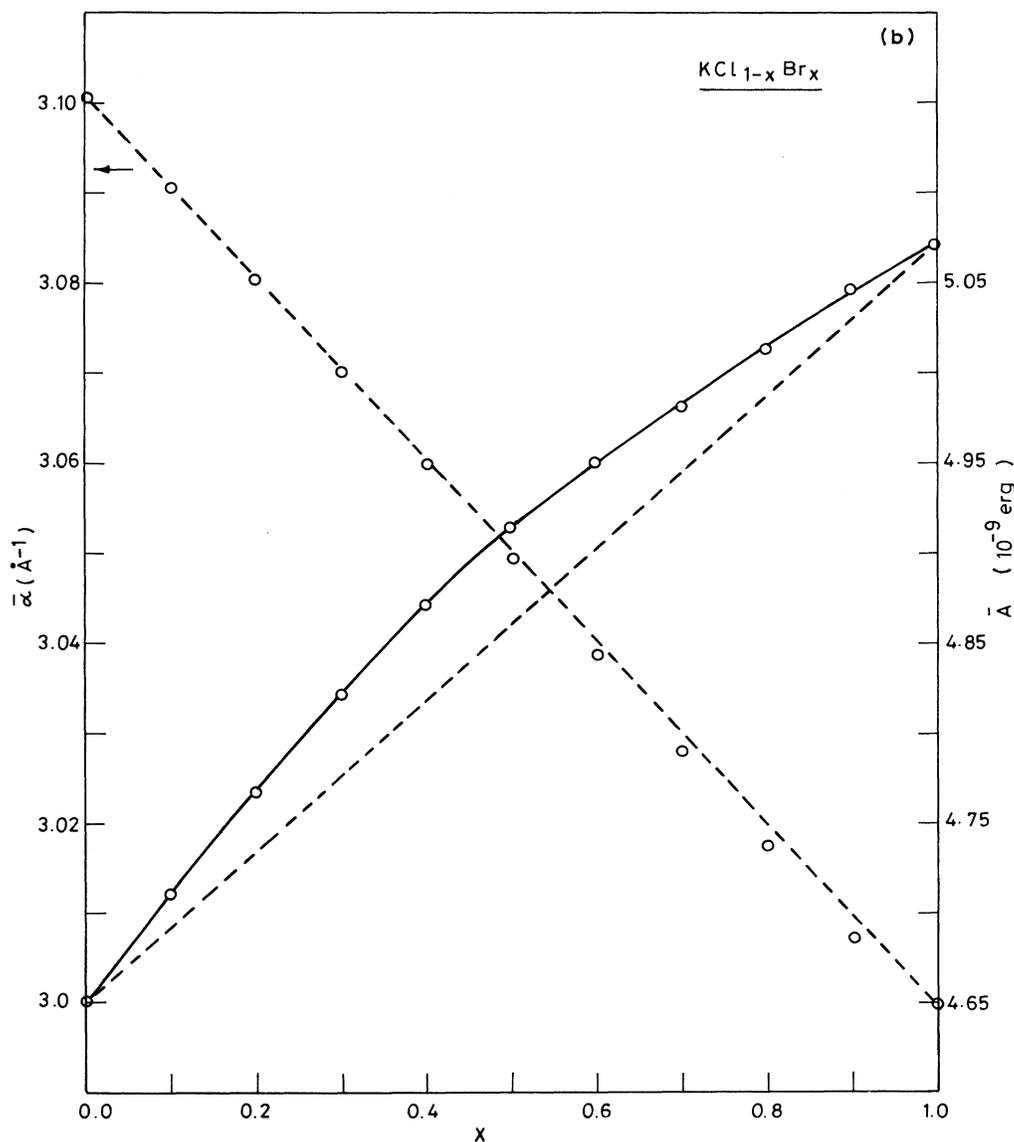


FIG. 3. (Continued).

where in the second equality is expressed as the unit-cell volume of the NaCl-type crystal structure.

The equilibrium condition to be satisfied by u is

$$\partial u / \partial R |_{R=R_c} = 0. \quad (4c)$$

h_c and ν_c are obtained through numerical derivatives of g_c with respect to T and P (see Fig. 1 and Appendix C). $\bar{\alpha}$ and \bar{A} can thus be completely determined from Eqs. (4a)–(4c). And with the help of 1f-AQH the equation of state of the solid solution can be worked out as a function of temperature and composition.

To check if T_c^{config} is lowered upon addition of vibrational contributions one must use, as is done here, the parameters determined at T_c^{config} . The results of the calculation of the parameters for the three systems $K_{1-x}Rb_xI$,

$KCl_{1-x}Br_x$, and $Na_{1-x}K_xCl$ are shown in Figs. 3(a)–3(c). These parameters depend on x , P , and T . Such a dependence follows from the cluster probabilities being dependent on x , P , and T . We have used the parameters corresponding to $P=0$ and $T=300$ K as this is closest to the experimental conditions. The compositional dependence indicates softening of effective interactions (follows from positive excess cluster energies).

It has been possible to compute the properties of the solid solution by taking into account the effect of quenching which can be compared with experimental measurements on quenched samples of solid solutions. Results for the system $Na_{1-x}K_xCl$ shown in Figs. 5(a) and 5(b) were obtained using the quenched parameter set [shown in Fig. 3(a)]. In practice, since $T_c^{\text{calc}} \neq T_c^{\text{expt}}$, the temperature from where quenching is done (usually to $T=300$ K)

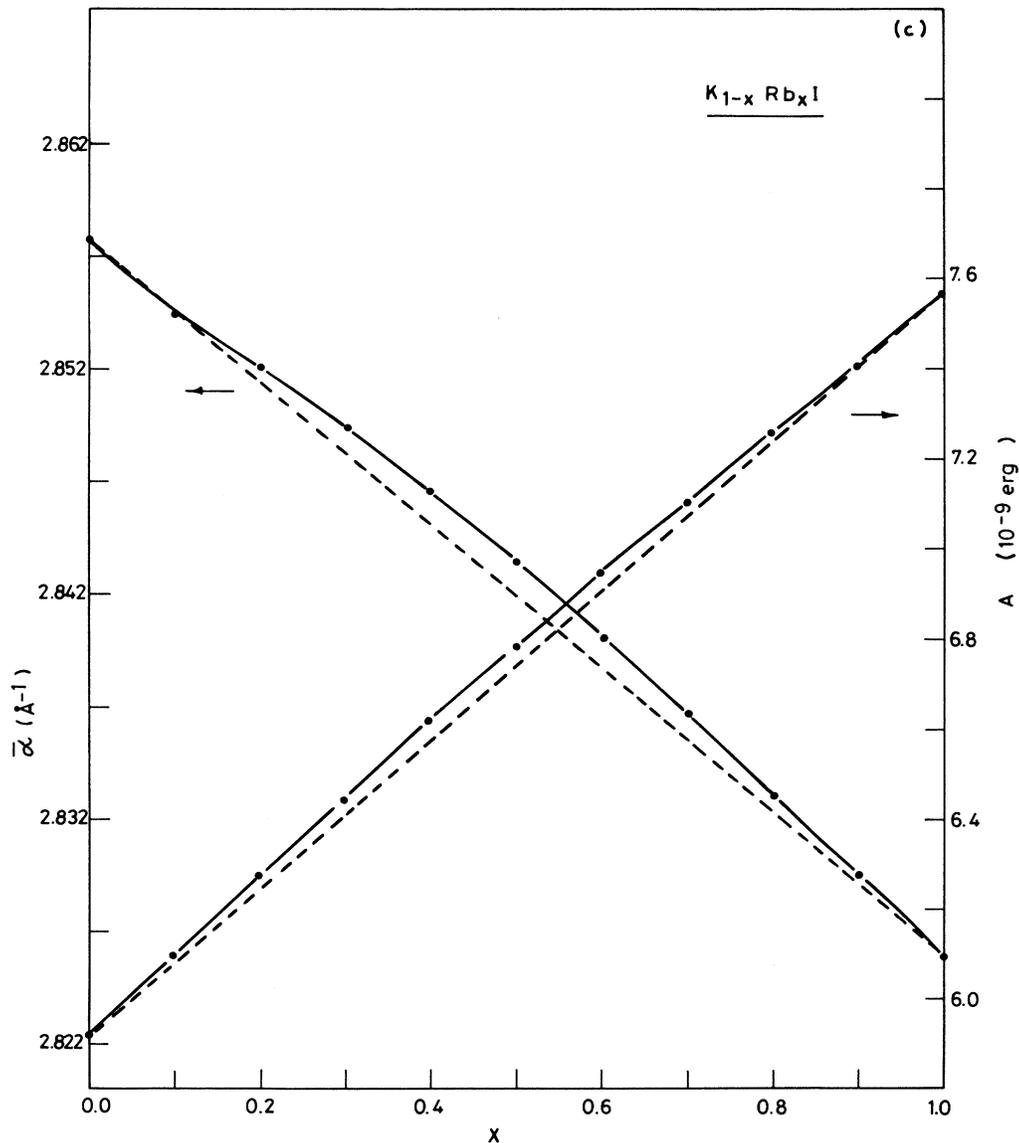


FIG. 3. (Continued).

differs in the calculation and experiment, becoming significant when T_c^{calc} deviates appreciably from T_c^{expt} .

The phase diagrams for the three systems, shown in Figs. 4(a)–4(c), have been obtained numerically from the excess free energy following the method of common tangents. Also included are the phase separation curves obtained from the excess configurational free energy. Results on the vibrational entropy, obtained through numerical differentiation of the free energy, are given in Table IV. Values of ω_{AQH} are obtained in the present work though EOS calculations at given x, T .

In general, we do not see any significant change in excess free energies and phase diagrams when vibrational contributions are included (magnitude is small as is clear

TABLE IV. Compositional dependence of excess vibrational entropy calculated at $T=300$ K.

x	Δs_{vib} (cal/mol,K)		
	$\text{K}_{1-x}\text{Rb}_x\text{I}$	$\text{KCl}_{1-x}\text{Br}_x$	$\text{Na}_{1-x}\text{K}_x\text{Cl}$
0.1	-0.0659	-0.0272	-0.0184
0.2	-0.1203	-0.0487	-0.0312
0.3	-0.1626	-0.0648	-0.3097
0.4	-0.1918	-0.0754	-0.0436
0.5	-0.2066	-0.0802	-0.0432
0.6	-0.2057	-0.0788	-0.0395
0.7	-0.1872	-0.0709	-0.0339
0.8	-0.1488	-0.0560	-0.0273
0.9	-0.0877	-0.0334	-0.0176

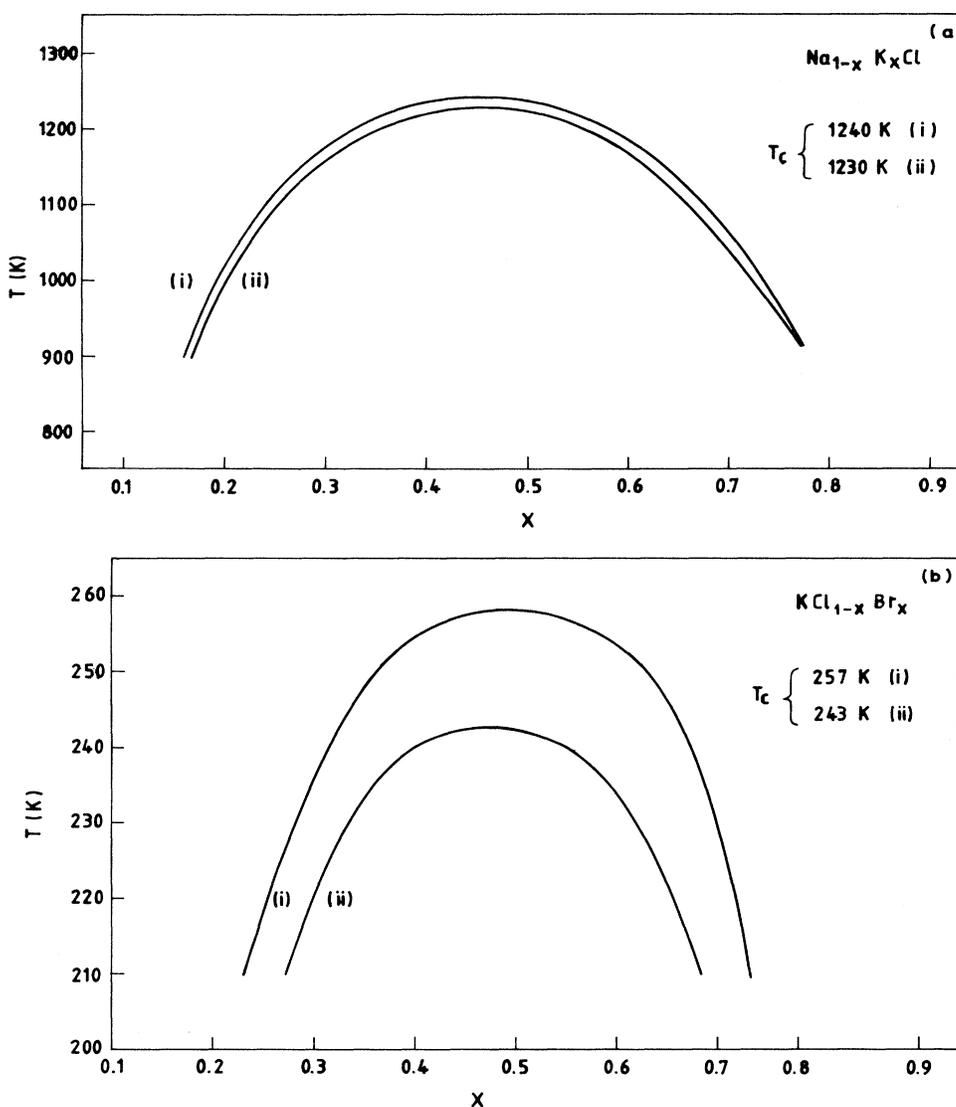


FIG. 4. Phase separation curves (i) and (ii) with and without vibrational corrections, respectively. While QCA has an intrinsic temperature scale, lack of a natural scale in equation of state calculations has led to a T_c for $\text{Na}_{1-x}\text{K}_x\text{Cl}$ higher than the melting temperatures of either end members. For the same reasons, as high temperatures are approached, $T_c^{\text{config+vib}}$ is deviating little from T_c^{config} .

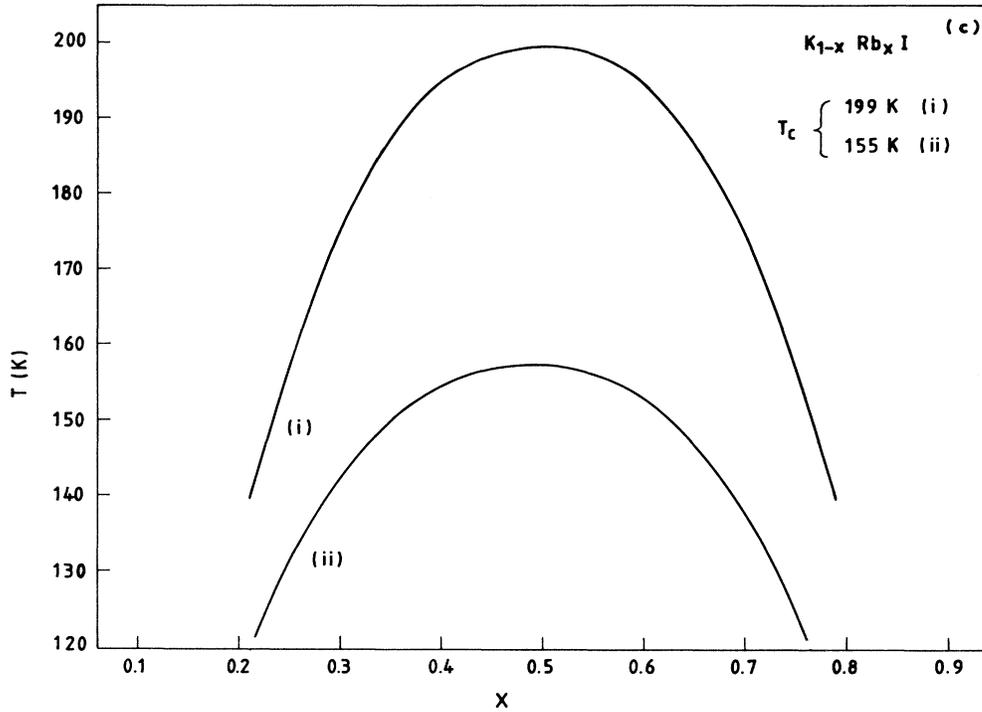


FIG. 4. (Continued).

from Table IV). We notice, however, that the addition of vibrational contributions to the configurational part seems to raise the critical temperatures instead of lowering it contrary to expectations.¹⁰ In order to have lower critical temperature, Δs_{vib} must be positive. In terms of the effective frequencies we must have $\Delta\omega_{\text{AQH}} < 0$ (for instance, from the expression for Δs_{vib} given in the introductory review, we see that at $x = \frac{1}{2}$, ω_{SS} should be smaller than the geometric mean of the frequencies of the end members). And lowering of the frequencies comes about through softening of interactions within the present model.

From Figs. 5(a) and 5(b) we see that, although lowering of ω_{AQH} is realized fully in $\text{Na}_{1-x}\text{K}_x\text{Cl}$, partly in $\text{KCl}_{1-x}\text{Br}_x$, it is not sufficiently negative. Nevertheless, as $\Delta\omega_{\text{AQH}}$ becomes relatively more negative, Δs_{vib} tends to be relatively more positive.

In paper II, we present the results of our calculation of physical properties of solid solutions. And we take up the effect of vacancies on the phase diagram.

APPENDIX A

Given the ion-ion potentials, the free energy within 1f-AQH can be written down as²⁸

$$F = N_0 \left[u + \beta^{-1} \sum_{k,\lambda} \ln(2 \sinh \xi_{k\lambda}) \right], \quad (\text{A1})$$

where

$$\xi_{k\lambda} = \frac{1}{2} \beta \hbar \omega_{k\lambda}$$

[for a diatomic crystal there are $6N_0$ vibrational modes labeled by the wave vector \mathbf{k} and branch (polarization) index λ] (N_0 is the Avogadro number). The summation is over the Brillouin zone (BZ). The average of the square of the frequencies over the BZ is defined as²⁸

$$\langle \omega^2 \rangle \equiv (6N_0)^{-1} \sum_{k,\lambda} \omega_{k\lambda}^2, \quad k \equiv |\mathbf{k}| \quad (\text{A2})$$

and with NN potentials the average is given by

$$\langle \omega^2 \rangle = (1/\mu) \nabla^2 v_{\text{NC}}, \quad (\text{A3})$$

where v_{NC} is the non-Coulombic potential and μ is the reduced mass. Explicitly,

$$\langle \omega^2 \rangle = (\alpha/\mu) \mathcal{A} e^{-\alpha R} (\alpha - 2/R) - (c_{+-}/R^8) - (d_{+-}/R^{10}). \quad (\text{A4})$$

The 1f-AQH approximation consists of replacing all the frequencies $\omega_{k\lambda}$ by a single frequency given by

$$\omega \simeq \langle \omega^2 \rangle^{1/2}. \quad (\text{A5})$$

The expression for free energy, per mole, becomes

$$f = F/N_0 = u + 6\beta^{-1} \ln(2 \sinh \xi), \quad \xi = \frac{1}{2} \beta \hbar \omega. \quad (\text{A6})$$

The equation of state is

$$P = - \{ \partial F / \partial V \}_T. \quad (\text{A7})$$

The bulk compressibility B_T is given by

$$B_T = V \{ \partial^2 F / \partial V^2 \}_T. \quad (\text{A8})$$

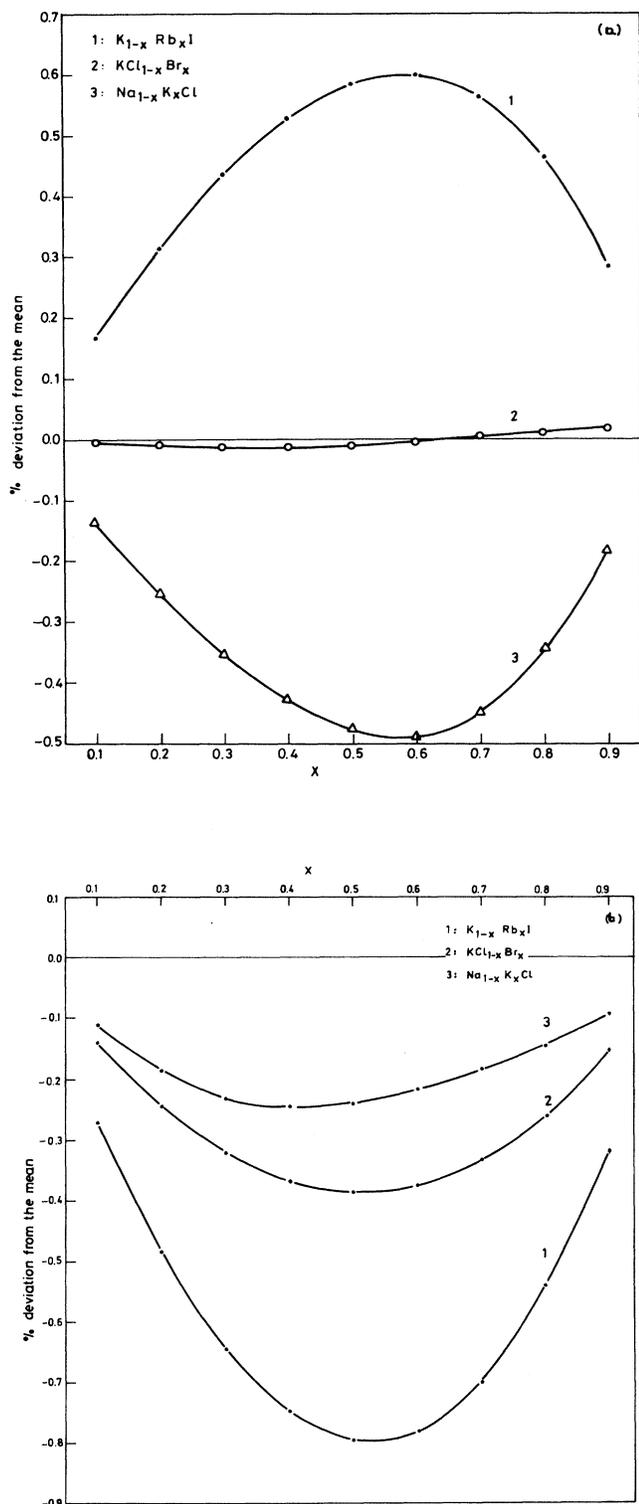


FIG. 5. (a) Compositional dependence of change in effective single frequency at $T=300$ K. Due to softening of repulsive interactions, there is a lowering of ω_{AQH} , but not for all three systems. (b) Compositional dependence of vibrational entropy at $T=300$ K. It is negative, but ends become relatively positive as $\Delta\omega_{AQH}$ becomes more negative.

We rewrite derivatives with respect to volume V , as those with respect to lattice parameter R .

For end members, an iterative procedure is used to obtain the potential parameters with input consisting of the experimental lattice parameter at equilibrium and the bulk modulus at the chosen temperature.

For solid solutions, we drop vdW terms and since the potential parameters would be known, the procedure to obtain the free-energy derivatives is just the inverse of what we had followed earlier.

APPENDIX B

The partition function for a given configuration $[p]$ is

$$Z_{\text{config}} = \sum_{[p]} W([p]) \exp\{-\beta\phi([p])\},$$

where W and ϕ in terms of $[p]$ are⁶

$$W = \frac{N!}{N_A!N_B!} \frac{\prod [Np_n^*]^{\alpha_n}}{\prod [Np_n]^{\alpha_n}}, \quad (\text{B1})$$

$$\phi = \sum \alpha_n p_n u_n. \quad (\text{B2})$$

p_n is the n -cluster occurrence probability defined as the ratio of the number of n -clusters to the total number of clusters. The normalization condition is

$$\sum_n \alpha_n p_n = 1. \quad (\text{B3})$$

The total number of B atoms in the configuration is obtained by counting the number of B atoms in all the clusters,

$$\sum_n (n/z) \alpha_n p_n = x = p_B (= N_B/N). \quad (\text{B4})$$

p_n^* denotes the random cluster occurrence probability and is defined as $p_n^* = (1-x)^z - n x^n$, $n=0,6$.

The most probable configuration, denoted by $[\bar{p}]$, is determined from the condition (the condition is equivalent to picking up the maximum term in the sum over configurations⁶)

$$\partial \ln Z_c([p]) / \partial [p] = 0 \quad \text{at } [\bar{p}]. \quad (\text{B5})$$

We solve Eq. (5) subject to the two conditions, Eqs. (3) and (4). We give the final expressions⁶ as follows: for $\{\bar{p}_n\}$ we have

$$\bar{p}_n = (\bar{p}_0^{(z-n)/z} \bar{p}_z^{n/z}) \exp(-\beta \epsilon_n), \quad (\text{B6})$$

$$\bar{p}_0 = p_A - \sum \frac{(z-n)}{z} \alpha_n \bar{p}_n, \quad n=1,5, \quad (\text{B7})$$

$$\bar{p}_z = p_B - \sum \frac{n}{z} \alpha_n \bar{p}_n, \quad n=1,5, \quad (\text{B8})$$

where we define the "excess" cluster energies $\{\epsilon_n\}$ as

$$\epsilon_n = u_n - \left[\frac{(z-n)}{z} u_0 + \frac{n}{z} u_z \right]. \quad (\text{B9})$$

$\varepsilon_0=0$ and $\varepsilon_z=0$ by definition.

From this result, we see that $\{\bar{p}_n\}$ is dependent on T . At high temperatures when $\beta\varepsilon_n \ll 1$, the temperature dependence will be small.

$$-\beta^{-1}\ln W([\bar{p}]) = \sum \alpha_n \bar{p}_n \varepsilon_n + \beta^{-1}\{(1-x)\ln[\bar{p}_0/p_0^*] + x \ln[\bar{p}_z/p_z^*] + (1-x)\ln(1-x) + x \ln x\} . \quad (\text{B10})$$

The excess configurational free energy, denoted by Δf_c , is defined as

$$\Delta f_c = f_c - [(1-x)u_A + xu_B] . \quad (\text{B11})$$

Recalling that x and $(1-x)$ can be expressed through Eqs. (3) and (4), we rewrite the first term in Eq. (10) and after simplification we get the result for Δf_c as

$$\Delta f_c = \beta^{-1}\{(1-x)\ln[\bar{p}_0/p_0^*] + x \ln[\bar{p}_z/p_z^*]\} + \beta^{-1}[(1-x)\ln(1-x) + x \ln x] . \quad (\text{B12})$$

This is the basic result of QCA.

APPENDIX C

Numerical calculations in the present work were done on a personal computer in FORTRAN with double precision. It was found that up to eight significant digits were essential for the iterations as we worked with cgs units all through and converted to calories in the end. Moreover, excess functions were evaluated, in cgs units,

The configurational free energy f_c per mole is

$$f_c[\bar{p}] = -\beta^{-1}\ln W([\bar{p}]) + \phi([\bar{p}]) .$$

The first term can be written as

when possible with explicit expressions for the differences instead of subtracting one large value from another. A step of 0.1 mole fraction was used to obtain the compositional dependence for the plots and tables. Where experimental data are available at arbitrary compositions, we have read off the present calculated values at those compositions from a plot and tabulated the results. For a single system a little over an hour is needed to perform all the computations, inclusive of all input and output operations between modules. Numerical derivatives of the Gibbs free energy, $G(P, T)$, were performed as follows.

With respect to T , Stirling's central difference tables were constructed with a step size of 0.001 K and the number of steps as nine. Five difference tables result.

With respect to T , Stirling's central difference tables were constructed with a step size of 0.001 K and the number of steps as nine. Five difference tables result.

With respect to P , $P=0$ is the starting point. We use Newton's forward difference table with a step size 1.01325×10^9 dyn/cm² (=1 kbar) and the number of steps five. Four difference tables result.

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