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Solid solutions of alkali halide compounds. II. Physical properties and vacancy contributions

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The advantages of describing solid solutions at each composition x and temperature T with effective interactions are illustrated by considering two issues in the present work: (1) Calculation of certain physical properties of interest at each x and T; and (2) handling of single impurities in a solid solution (the formation energy of Schottky defects has been estimated). Our results suggest that significant contributions to the total entropy of a solid solution can arise from configurational entropy due to vacancies.

I. INTRODUCTION

Various physical properties of interest, such as the bulk modulus, elastic constants, and thermal expansion coefficient, can be obtained through appropriate derivatives of the free energy—such calculations have been done for elemental solids and stoichiometric compounds.[1-3] For solid solutions there has been no model that permits properties to be computed as derivatives of the free energy. Interpolatory schemes exist though, for estimating the compositional dependence of certain properties using the corresponding values for the end members.[4-9] In particular, there are two properties, often used in estimates as a linear function of composition x, which have neither been verified nor found to be consistent amongst each other through any explicit model calculations (1,2 below refer to end members).

(a) Volume: $V(x)=(1-x)V_1+xV_2$ (Vegard's law[10,11]). This kind of dependence has also been used for the lattice parameter R.

(b) Force constant: $f(x)=(1-x)f_1+xf_2$.

We may anticipate simple averages over higher derivatives of energy (force constants, bulk modulus, thermal expansion coefficient, etc.) to be a good approximation for estimating the energy—provided, experimentally the higher derivatives deviate little from a linear dependence on x.

However, since microscopic averages are superior to macroscopic averages the problem will be to average the interaction energies and their derivatives over A and B species atomistically dispersed in a solid solution.

II. PRESENT CALCULATIONS

We parametrize the configurational energy of the solid solution through effective potentials and with the help of the quasiharmonic approximation perform the equation of state calculations at (x,T) in just the same way crystalline solids are treated (see paper I).

The free energy and its derivatives are evaluated numerically (details are given in I). Quantities such as the elastic constants and electric susceptibility can also be obtained by direct numerical differentiation—through differentiation of the Gibbs free energy in the presence of stress and electric fields, respectively. However, the change in the free energy was small for numerical purposes and we could only evaluate the explicit expressions available for such quantities based on interionic potentials,[12] neglecting configurational contributions. We note that the set $[p^*]$ of random cluster probabilities does not depend on any of the external fields including pressure and temperature. And so, when $[\bar{p}]$ tends to $[p^*]$ at high temperatures, configurational contributions to the free-energy derivatives with respect to external fields drop off.

The results are presented in Figs. 1–3 and Tables I–VI along with experimental results and calculations where available.[13-25]

III. DATA PRESENTATION

The compositional dependence of physical properties at various temperatures is of primary interest whether calculated from a model or obtained from experiment. The following procedure is employed for presenting the results: First, excess functions are defined in the usual manner,[26] as

$$\Delta q(x,T)=q(x,T)-[(1-x)q(0,T)+xq(1,T)] ,$$

where q is any given property in the solid solution and the quantity in the square brackets is the mean—a weighted sum, pertaining to a mechanical mixture of the end members at the same temperature:

$$q(0,T)\equiv q_A(T), \quad q(1,T)\equiv q_B(T) ,$$

A and B referring to end members.

Next, the percentage deviation from the mean is defined through the ratio of the excess over the mean. Such a definition makes it possible to compare any two models as well as a model with experiment for different systems. The reason is that a model's description of a real system is approximate and hence end-member properties are only approximately determined—this means that the "base-line" is model dependent. This in turn affects the excess functions directly. Further, since experiment deals with real systems, a comparison with model calculations must be free from direct base-line effects. As indicated above, and as can be seen from the definition of percentage deviation from the mean, a model can be assessed in two ways—one, in its ability to describe the end members (base line) correctly, and two, in its ability to give the deviations from the mean correctly. We note that for consistency, a model should describe the end members also instead of taking the real systems as they are. Accordingly, the figures and tables contain results in terms of percentage deviations from the mean where necessary.

IV. RESULTS AND DISCUSSION

There are two general features against which our results are discussed.

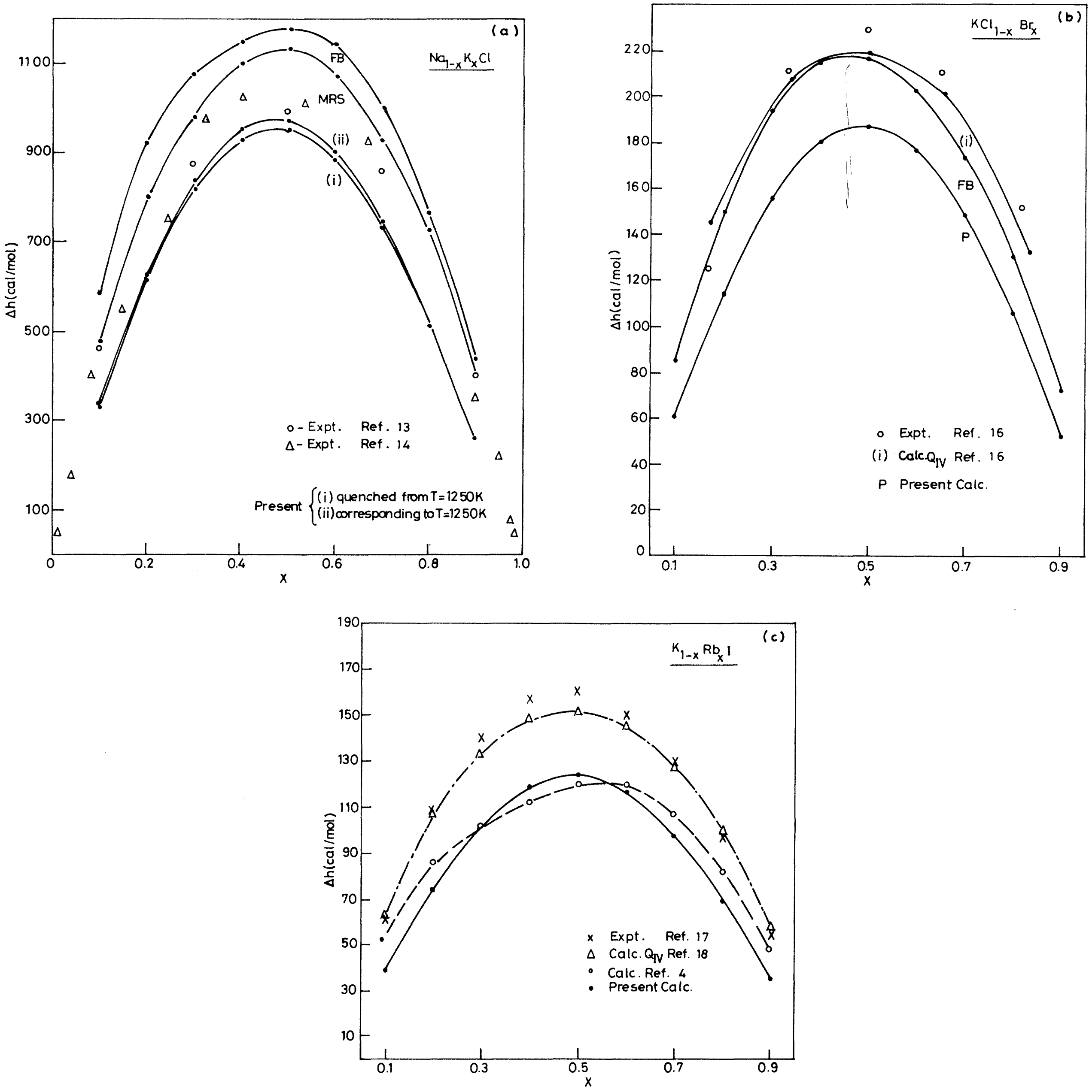

FIG. 1. (a) Composition dependence of excess enthalpy Δh. FB refers to the work of Fancher and Barsch, Ref. 4. MRS refers to the work of Maity, Roy, and Sengupta, Ref. 15. (b) Composition dependence of excess enthalpy Δh. FB refers to the work of Fancher and Barsch, Ref. 4. (c) Composition dependence of excess enthalpy Δh. (a)–(c): compositional dependence of excess enthalpy Δh (heats of formation). (a) as $T_c > 300$ K for this system, we calculate Δh both at T_c and at 300 K with the "quenched" set. Note that in all the figures experiment refers to measurements made at 298 K and 1 atm pressure while the present calculations (as well as those of others referred to here) are done at 300 K with the pressure set to zero. It is clear that NN bond length changes account for nearly 90% of the contributions to excess enthalpy. Thermal corrections do not exceed 10% at the maximum in any system.

(1) It is expected on general grounds that when the excess volume of the solid solution is positive, the following inequalities would be satisfied:[27,28] if

$$\Delta v > 0$$

then

$$\Delta B_T < 0, \quad \Delta\omega_{\text{eff}} < 0, \quad \Delta s_{\text{vib}} > 0 \ .$$

ω_{eff} is an effective frequency characteristic of the system which can be related to Debye temperature, for instance. We can also infer $\Delta(\text{force constant}) < 0$, $\Delta C_{11} < 0$, $\Delta C_{12} < 0$ to be satisfied following the above relations.

(2) For systems with $\Delta h > 0$ the use of the quasichemical approximation or cluster variation method will lead to a configurational entropy that is less than ideal mixing entropy[26] (see I).

In the present model, the excess enthalpy results [in Figs. 1(a)–1(c)] are of the right order of magnitude while the configurational entropy values are significantly lower than the ideal mixing entropy values. The discrepancy is maximum for the high-temperature system $\text{Na}_{1-x}\text{K}_x\text{Cl}$ [$T_c^{\text{expt}} \simeq 800$ K (Ref. 29)]. The values of T_c that would result if a regular solution model were used, with Δh_{calc} from the present model, are higher ($T_c = 2\Delta h / k_B$ in the regular solution model at $x = 0.5$). In fact, if Δh_{expt} is used, the resulting T_c value is again higher than T_c^{expt}. This clearly shows that the ideal entropy values are inadequate. We can see that the errors in the calculation of Δh values are far less significant than the errors in entropy calculation. In order to get reasonable values for T_c, additional sources for entropy are sought. Two such are the vibrational entropy and the entropy due to vacancies.

If $\Delta s_{\text{vib}} > 0$ as expected, it can bring the total calculated entropy ($\Delta s_{\text{config}}^{\text{QCA}} + \Delta s_{\text{vib}}$) towards and perhaps beyond the ideal mixing entropy. We estimate Δs_{vib} through the Debye temperature Θ_D along with a similar estimate from the Debye temperatures deduced from experiment[11] (Table IV). It is worth noting that even if $\Delta s_{\text{vib}} > 0$ is achieved in such a way that T_c^{calc} is brought down to realistic values, the possibility of $T_M^{\text{calc}} > T_M^{\text{expt}}$ (T_M denotes melting temperature) for end members can still exist—this implies that a correct description of end members would help in determining Δs_{vib} better as we would be using the same improved equation of state (EOS) for intermediate compositions as well.

The other inequalities turn out to be as expected for most of the quantities calculated. The discrepancy between calculated and measured values of various properties (we refer to the percentage deviations from the mean of the properties where applicable) is discussed below.

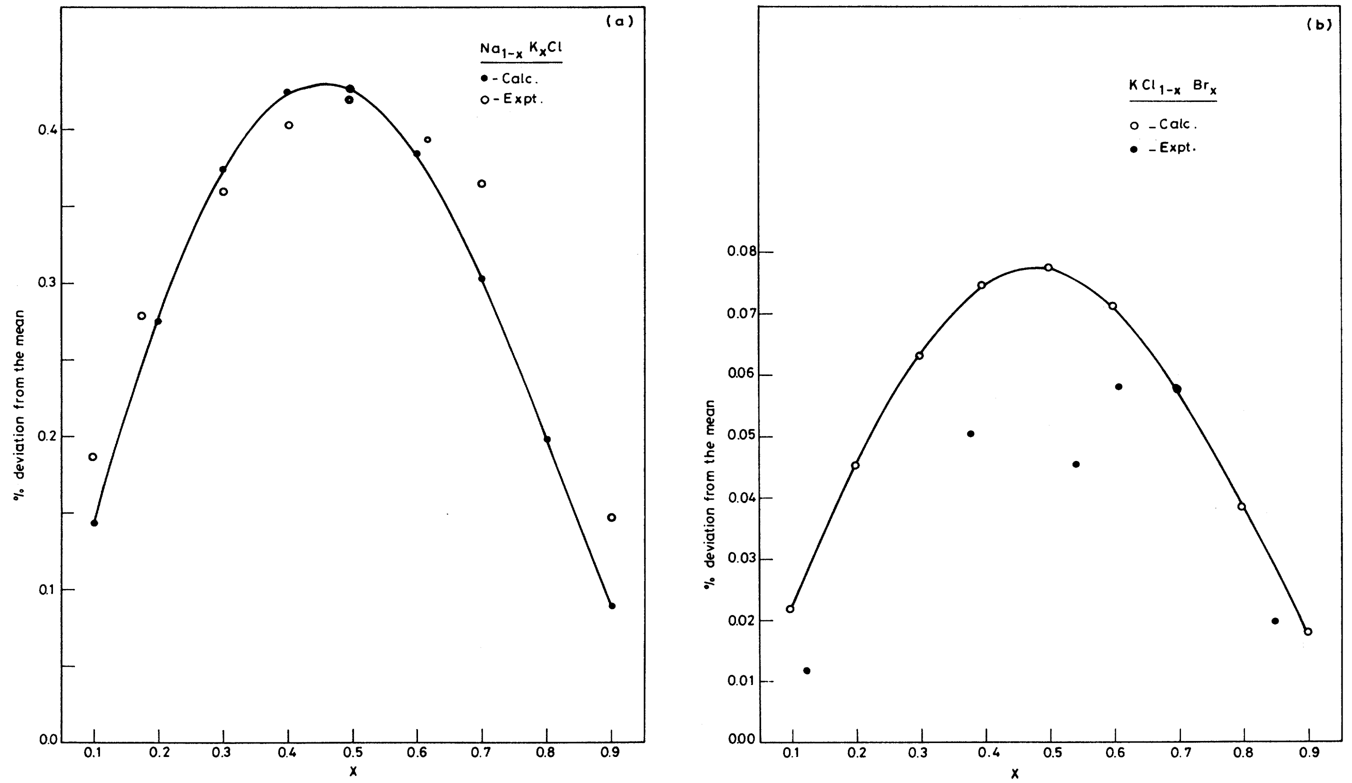

FIG. 2. (a) Compositional dependence of lattice parameter. Experimental data, taken from Ref. 13, refers to measurements on a quenched sample quenched to $T = 298$ K. Calculation was done with the "quenched" set corresponding to $T = 300$ K. (b) Compositional dependence of lattice parameter at $T = 300$ K. Experimental data taken from Ref. 19 corresponding to $T = 298$ K.

Although the enthalpy is obtained as a T derivative of the free energy in the present calculation, since thermal energy contributions are not significant as noted earlier, the total is close to the result from the quasichemical approximation (QCA) (this is not the case for all other properties such as volume, bulk modulus, etc.). In any case, the calculated enthalpy values ($P=0$) are lower than measured values ($P=1$ atm). That it is lower is a point worth noting, keeping in mind that the present model as well as most of the other estimates include only nearest-neighbor (NN) interactions. The first P derivative, volume, agrees fairly well with experiment. The second P derivative, bulk modulus, and the elastic constants (without thermal energy corrections) are systematically lower than the measured values. The changes in the elastic properties due to vacancies and dislocations could be the main reason for this lowering (that these defects contribute appreciably has been noted by Goland;[30] that vacancies and dislocations occur in greater numbers in solid solutions emerges from the review of Haribabu and SubbaRao[10]). The values obtained through interpolation schemes ought to be low, as we find, for this same reason.

The calculation of $\Delta\epsilon_0$ and $\Delta\epsilon_\infty$ from the present model is mainly intended to determine the effect of the compositional dependence of volume and force constant, present in the simple expressions for ϵ_∞ and ϵ_0 based on the point polarizable ion approximation. The Clausius-Mossotti relation is used for ϵ_0 and ϵ_∞. The results of present calculations on $\Delta\epsilon_0$ and $\Delta\epsilon_\infty$ are given in Figs. 3(f) and 3(g) and Table VI. We have assumed that there is no change in the polarizability of individual ions. This assumption, though consistent with the use of a crystal-independent set of polarizabilities (the set we have used is given in Table VII), may be inadequate for solid solutions where we expect the ions to be sensitive to local disorder.[31]

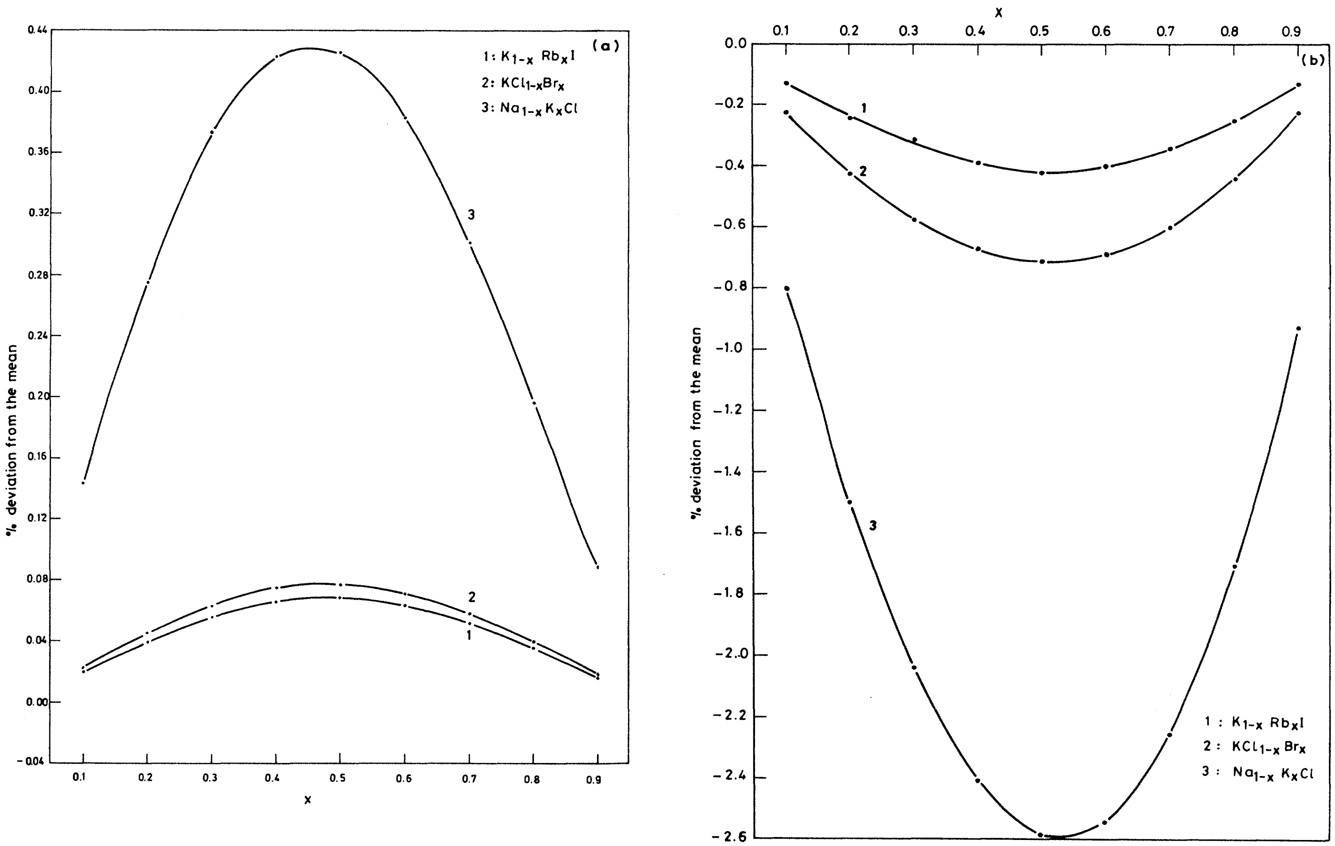

FIG. 3. (a) Compositional dependence of lattice parameter. (b) Compositional dependence of bulk modulus. (c) Compositional dependence of force constant. (d) Compositional dependence of elastic constant C_{11}. (e) Compositional dependence of elastic constant C_{12}. (f) Compositional dependence of static dielectric constant. (g) Compositional dependence of high-frequency dielectric constant. (h) Compositional dependence of Schottky defect formation energy. (a)–(h): Compositional dependence of certain physical properties of the three systems expressed in terms of percentage deviations from the mean corresponding to $T=300$ K. For $Na_{1-x}K_xCl$, the "quenched" set was used. A small but definite asymmetry in the compositional dependence can be seen. The trend shown by the three systems for most of the physical properties is characteristic—end-member pairs having greater disparity in bond strengths and bond lengths display larger percentage deviations from the mean. The trend shown in elastic properties, namely, the calculated changes in the magnitude being smaller than measurements, is consistent with our other results, all of which indicate inadequate softening of the repulsive interactions.

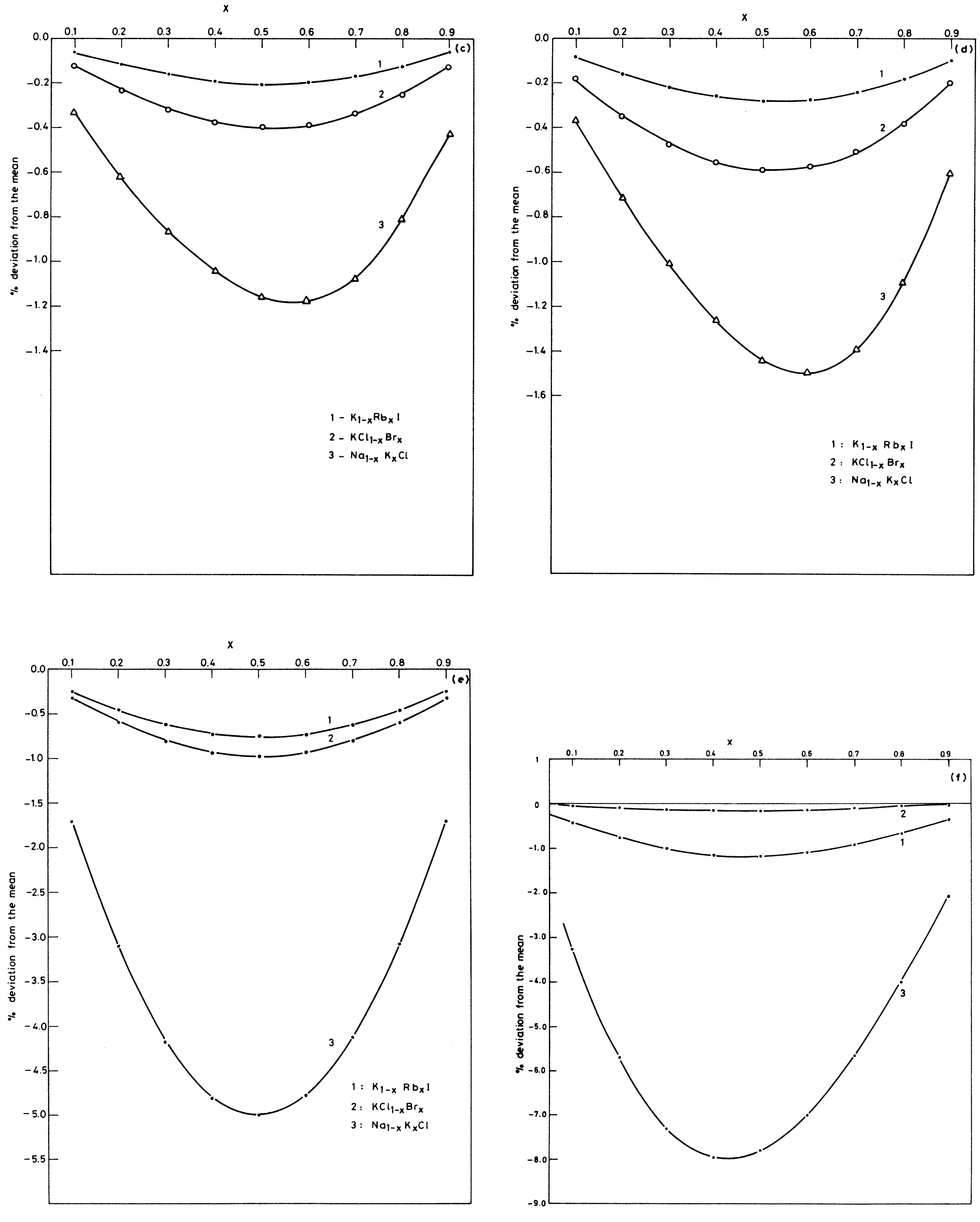

FIG. 3. (Continued).

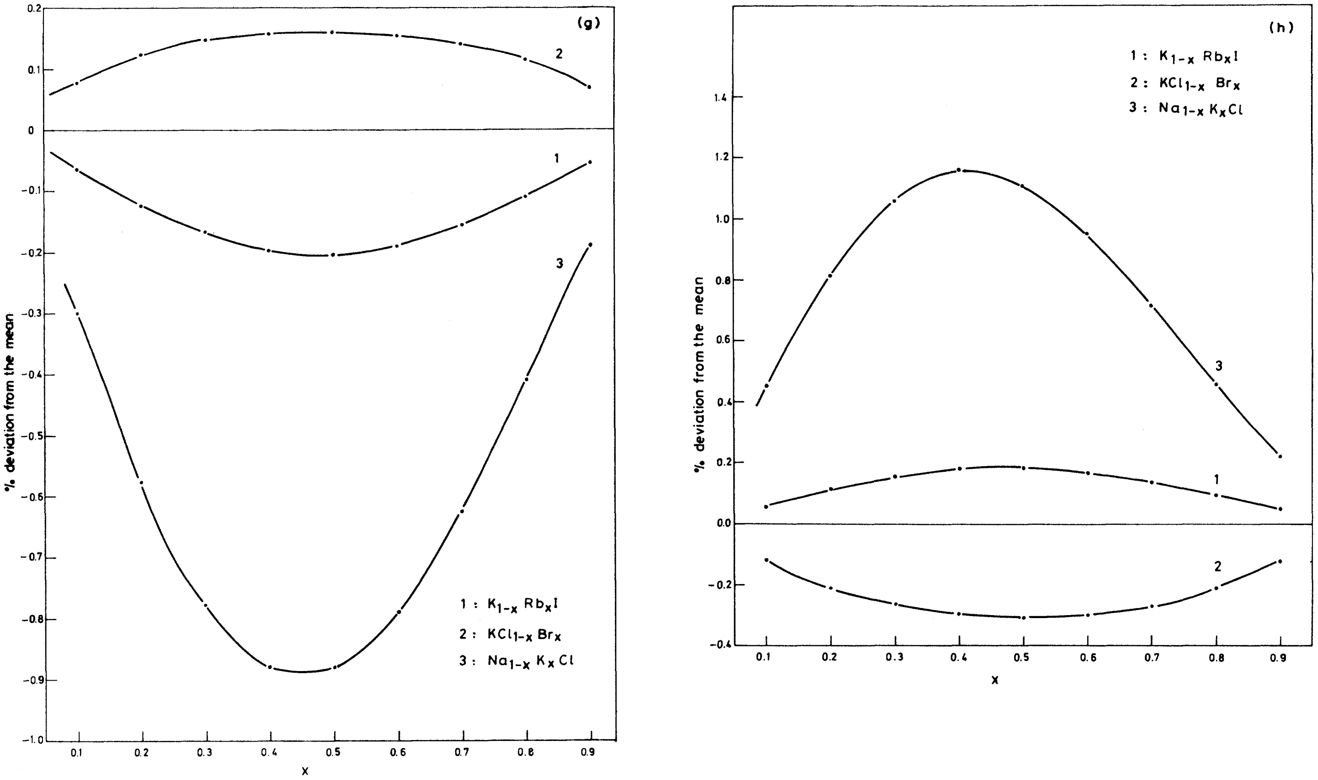

FIG. 3. (Continued).

V. THERMAL POINT DEFECTS

The role of thermal defects assumes greater significance in solid solutions at high temperatures. Although there is no successful theory for melting of elemental solids and stoichiometric compounds, a high thermal defect concentration is believed to exist close to the melting point.[32] It is therefore of interest to know the defect structure in solid solutions and their relation to solidus and liquidus temperatures.

We note, however, that we would only be dealing in the present work with "one-phase" theories. That is, we can, at most, study the stability of a single phase without being able to describe the crossover to the second phase (liquid; further, the low-temperature two-phase structure of the solid solution cannot be described by the one-phase theories, for a different reason though). It may be possible, however, to discuss precursive phenomena associated with the approach to the crossover.[32] In this sense then, we ask the following question: Will the intrinsic concentration of thermal point defects be larger in solid solu-

TABLE I. Compositional dependence of lattice spacing, for the system $K_{1-x}Rb_xI$, expressed in percentage deviation from the mean. Experimental data taken from Ref. 20.

	ΔR	
x	Calc. ($T=300$ K)	Expt. ($T=298$ K)
0.13	0.026	0.051
0.25	0.048	−0.028
0.38	0.064	−0.006
0.5	0.068	0.222
0.6	0.063	0.111
0.7	0.051	0.11
0.78	0.038	0.13
0.9	0.017	−0.06

TABLE II. Compositional dependence of bulk modulus, for the system $KCl_{1-x}Br_x$, expressed as percentage deviation from the mean. Included is the set calculated by Varotsos and Alexopoulos (VA), Ref. 5. Experimental data taken from Slagle and McKinstry's work, Ref. 21.

		ΔB_T	
x	Present calc. ($T=300$ K)	VA ($T=298$ K)	Expt. ($T=298$ K)
0.168	−0.368	−0.549	−0.831
0.171	−0.374	−0.833	−0.732
0.382	−0.664	−0.708	−1.562
0.387	−0.668	−0.45	−1.445
0.578	−0.701	−0.518	−1.468
0.598	−0.691	−0.668	−1.71
0.795	−0.455	+0.041	−0.645
0.8	−0.449	+0.213	−0.95

TABLE III. Compositional dependence of elastic constants C_{11} and C_{12}, for the system $KCl_{1-x}Br_x$, expressed as percentage deviation from the mean. Calculations were done at $T = 300$ K; room-temperature experimental data taken from Ref. 21.

	ΔC_{11}		ΔC_{12}	
x	Calc.	Expt.	Calc.	Expt.
0.168	−0.294	9.976	−0.519	14.28
0.171	−0.3	9.836	−0.527	14.71
0.382	−0.542	−25.25	−0.912	4.437
0.387	−0.546	1.66	−0.918	4.646
0.578	−0.583	−3.941	−0.944	−3.617
0.598	−0.575	−5.158	−0.931	−4.304
0.795	−0.385	−10.18	−0.604	−10.11
0.8	−0.378	−10.23	−0.592	−11.65

tions than in corresponding end members? If we assume, for vacancies in a solid solution, an average Gibbs free energy of formation g_f, then the question can be rephrased as the following: Will g_f be lowered in solid solutions?

We have chosen to estimate vacancy formation energy for two reasons.

(1) To illustrate the scope of the model for single defect calculations in solid solutions.

(2) To check if vacancy concentration is enhanced in the solid solution—enhancement is expected since the stresses in the solid solution can be relieved by creating vacancies, which means that the vacancy formation energy can be lowered.

Realistic single defect calculations in solid solutions are difficult because the equilibrium positions of the ions before a defect is introduced are not known and consequently, relaxation to the final equilibrium positions cannot be determined.[33] In a binary solid solution, since there are two types of atoms A and B in a variety of environments, we can expect a distribution of vacancy formation energies. It is not clear if this distribution will be bimodal in nature. Bimodal distribution, even if we succeed in obtaining it, presents difficulties in the interpretation of experiments.

TABLE V. Comparison between calculation and experiment of the Schottky defect formation energy expressed in eV.

	h_S (eV)				
Method	NaCl	KCl	KBr	KI	RbI
Calc.	2.566	2.591	2.355	2.08	2.10
Expt.	2.55[a]	2.57[a]	2.49[a]	2.31[a]	2.10[b]

[a] Reference 24.

[b] Reference 38.

The present model for the solid solution, in the parametrized form, can be used to compute vacancy formation energy just as it would be done in the case of end members. What we get from this model can be taken to be the averaged free energy (with vibrational contributions neglected). The vacancy formation energy is defined as

$$h_s = W_v^+ + W_v^- - W_L \ ,$$

where $W_v^{\pm}$ denotes the work done to create a vacancy at the cation or anion site and W_L is the lattice energy per pair. We make use of a simple procedure[34] to evaluate, to first order, this quantity. The expression involves quantities all of which are composition dependent and can be evaluated within the present model.

There will be a configurational or mixing entropy change associated with the formation of n vacancies given by

$$\Delta s_{\text{config}} = k_B \ln(W'/W) \ ,$$

where W' and W are the number of configurations with and without vacancies. For a perfect crystal, W is taken to be unity (this means that the "ground state" chosen is unique with all sites occupied). To treat vacancies in solid solutions we must define the corresponding W carefully.

The excess or change in the configurational entropy due to the vacancies, with respect to the end members, can be written as

TABLE IV. Compositional dependence of vibrational frequencies and excess vibrational entropy. Comparison between estimates made using the present values of ω_{AQH} and Θ_D deduced from experiments for the system $KCl_{1-x}Br_x$ at room temperature. The second half of the table was obtained by making use of the relation between Θ_D and ω_{AQH} given above. As noted earlier, the present values for ω_{AQH} are not lowered to a sufficient extent.

	Δs_{vib} (in cal/mol, K)			% deviation from the mean, of vibrational freq.		
x	a	b	c	a	b	c
0.268	0.143	0.134	−0.047	−1.768	−1.71	−0.012
0.382	0.288	0.222	−0.074	−3.389	−2.88	−0.012
0.598	0.248	0.123	−0.076	−3.123	−2.135	−0.002
0.8	0.172	0.122	−0.048	−2.176	−1.792	0.012

[a] Using Θ_D from specific-heat data of Karlsson, Ref. 22.

[b] Using Θ_D from elastic-constant data of Nagaiah and Sirdeshmukh, Ref. 23.

[c] Θ_D was obtained from the relation $\Theta_D = \frac{4}{3}\Theta_E$, where $\Theta_E = \hbar\omega_{\text{AQH}}/K_B$.

TABLE VI. Comparison between experiment ($T=298$ K) and calculation ($T=300$ K) on the compositional dependence of high-frequency dielectric constant ϵ_∞ expressed in percentage deviation from the mean. In columns 2–5 the Clausius-Mossotti relation, $(\epsilon_\infty-1)/(\epsilon_\infty+2)=(4\pi/3v)(\alpha_+ + \alpha_-)$, is used for calculations. $\alpha_\pm$ is the electronic polarizability of cation and anion, respectively. Values are taken from Ref. 25. For the solid solution $KCl_{1-x}Br_x$, $\alpha_+=\alpha_{K^+}$, $\alpha_-=(1-x)\alpha_{Cl^-}+x\alpha_{Br^-}$ $(0\le x\le 1)$. v is the unit-cell volume. In (a) and (b) $R(x)$ was taken as $R(x)=(1-x)R_{KCl}+xR_{KBr}$ with the end-member lattice parameters from the present calculation (a) and experiment (b), respectively. The experimental refractive indices at these compositions were taken from the work of Nigara and Kamiyoshi, Ref. 8. (c) is deduced from their calculations. We note that the simple estimates in (a) and (b) are close to (c), all of them being higher than the present calculations.

			$\Delta\epsilon_\infty$			
x	$[\bar{p}]$	$[p^*]$	(a)	(b)	(c)	Expt.
0.2	0.122	0.121	0.212	0.212	0.228	0.056
0.4	0.158	0.153	0.311	0.319	0.339	0.352
0.6	0.155	0.15	0.303	0.312	0.323	0.123
0.8	0.115	0.115	0.197	0.203	0.215	−0.312

$$\Delta S_v^{\text{excess}}=Nk_B\left[(1+x_v)\ln(1+x_v)-\sum_{i=A,B}x_i(1+x_v^i)\ln(1+x_v^i)\right]-Nk_B\left[x_v\ln x_v-\sum_{i=A,B}x_ix_v^i\ln x_v^i\right],$$

where the second term in each of the large parentheses accounts for vacancies in the end members. Considering the simple case of vacancies in an $A_{1-x}B_x$ type solid solution, we define the Gibbs free energy of formation of vacancies in each case as Δg_v^A and Δg_v^B for the A and B end members, $\Delta g_v^{ss}(x)$ in the solid solution at overall composition x ($x=N_B/N$). We start with $(N+n)$ sites, N_A, N_B atoms of type A and B and n vacancies. The total number of ways of arranging these among $(N+n)$ sites is

$$W_v=N_S!/(n!N_A!N_B!),\quad N_S=(N+n).$$

We write $n=x_vN$ such that $N_S=N(1+x_v)$.

The entropy S_v is given by $S_v=k_B\ln W_v$. Using Stirling's approximation and after simplification we have

$$S_v=-Nk_B(x_A\ln x_A+x_B\ln x_B)+Nk_B\ln(1+x_v)$$
$$-Nk_B[x_v\ln x_v-(1+x_v)\ln(1+x_v)],$$

where $N_i/N_S=N_i/(N+n)=N_i/[N(1+x_v)]=x_i/(1+x_v)$, $i=A,B,v$. N_v is number of vacancies, indexed by v. When there are no vacancies only the first term in S_v remains. To get the excess we subtract the ideal entropy of mixing from S_v.

TABLE VII. Crystal-independent set of electronic polarizabilities assigned to the cations and anions. From Jaswal and Sharma, Ref. 25.

Compound	α_+ (10^{-24} cm^3)	α_-
NaCl	0.29	2.947
KCl	1.133	
KBr		4.091
KI		6.116
RbI	1.679	

This expression permits an estimate of $\Delta S_v^{\text{excess}}$ if the Δg_v's are known in the three cases. It has been pointed out[35,36] that (i) the above expression for $\Delta S_v^{\text{excess}}$ leads to the result that a $>1\%$ excess of vacancies in the solid solution can contribute significantly through the corresponding configurational entropy term and (ii) experimental values for the total excess entropy obtained from activity coefficient measurements along with Wasastjerna's Q_{IV} approximation[37] are seen to exceed that of ideal mixing entropy. However, it is not clear if vacancies can contribute thus at low temperatures ($\simeq 300$ K), although it has been suggested in the literature that, for systems like $K_{1-x}Rb_xI$ and $KCl_{1-x}Br_x$, they can do so.[10]

The results are presented in Table V for end members along with experimental values, and in Fig. 3(h) for the compositional dependence.

Of the three systems studied, only for $KCl_{1-x}Br_x$ does the excess vacancy formation energy become negative and that to a small extent (the excess entropy due to vacancies in this case was found to be even less significant). These results must be regarded as preliminary in nature. The calculation of the Schottky defect formation energy, which in the present work depends on $\epsilon_0, \epsilon_\infty$, volume and force constant, must be treated on the same footing as the calculation of ϵ_0 and ϵ_∞.

When $\Delta\epsilon_\infty>0$, $\Delta h_s<0$ obtains as in the case of $KCl_{1-x}Br_x$ [Figs. 3(g) and 3(h); Fig. 3(g) shows $\Delta\epsilon_0$ close to the zero axis]. This kind of correlation can perhaps be used to guess at the sign of Δh_s from $\Delta\epsilon_0, \Delta\epsilon_\infty$ through experiment.

VI. CONCLUSIONS

We have the following.

(a) The interactions neglected, though important in their own right, are not as crucial as obtaining an improved EOS which ought to, even with restricted interactions, describe high-temperature behavior better.

(b) The entropy contributions from atomic vibrations and vacancies are significant and can, together with configurational entropy from the QCA or the cluster variation method (CVM), approach and even exceed the ideal entropy of mixing. And it is important for a model to account for these two contributions.

(c) It would be of interest to correlate the measured compositional dependence of the excess static dielectric constant ($\Delta\epsilon_0$) with that of the excess Schottky defect formation energy (Δh_s) (to check if $\Delta h_s < 0$, when $\Delta\epsilon_0 > 0$; $\Delta h_s < 0$ leads to an excess vacancy concentration in the solid solution).

(d) To get an idea of the distribution of the formation and migration energies of Schottky defects an analysis of the measured compositional dependence of (i) total vacancy concentration, (ii) ionic conductivity, and (iii) self-diffusion coefficients of the three species A, B, and C (in $A_{1-x}B_xC$) may perhaps be necessary. We expect that while dilatometric studies may perhaps give only the total number of vacancies present, self-diffusion experiments would be more sensitive to vacancy characteristics in solid solutions.

The physical properties of solid solutions are expected to be sensitive to defect microstructure. And, to model impurities such as color centers and to consider the microstructure of a solid solution, we hope that an averaged system is a good point of departure.

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[1] D. C. Wallace, *Thermodynamics of Crystals* (Wiley, New York, 1972).

[2] A. I. Kitaigorodsky, *Molecular Crystals and Molecules* (Academic, New York, 1973).

[3] A. J. Pertsin, J. Phys. Chem. Solids **46**, 1019 (1985).

[4] D. L. Fancher and G. R. Barsch, J. Phys. Chem. Solids **30**, 2503 (1969).

[5] P. Varotsos and K. Alexopoulos, J. Phys. Chem. Solids **41**, 1291 (1980).

[6] J. Shanker and G. D. Jain, Phys. Rev. B **27**, 2515 (1983).

[7] C. Basu, A. Kanrar, and U. S. Ghosh, Phys. Status Solidi B **114**, 221 (1984).

[8] Y. Nigara and K. I. Kamiyoshi, Bull. Res. Inst. Sci. Meas. **19**, 135 (1971).

[9] P. Varotsos, Phys. Status Solidi B **100**, K133 (1980).

[10] V. Haribabu and U. V. SubbaRao, Prog. Crystal. Growth. Charact. **8**, 189 (1984).

[11] D. B. Sirdeshmukh and K. Srinivas, J. Mater. Sci. **21**, 4117 (1986).

[12] The expressions used here are found in Ref. 1 above.

[13] W. T. Barrett and W. E. Wallace, J. Amer. Chem. Soc. **76**, 366 (1954).

[14] M. W. Lister and N. F. Meyers, J. Phys. Chem. **62**, 145 (1958).

[15] S. N. Maity, D. Roy, and S. Sengupta, Phys. Status Solidi B **99**, 327 (1980).

[16] V. Hovi, Soc. Scien. Fenn. Commun. Phys. Math. XV **12**, 1 (1950).

[17] G. R. Allakhverdov, N. I. Sorokin, and B. D. Stepin, Russ. J. Phys. Chem. **49**, 1789 (1975).

[18] L. L. Makarov and D. Yu. Stupin, Russ. J. Phys. Chem. **35**, 363 (1961).

[19] O. D. Slagle and H. A. McKinstry, Acta Crystallogr. **21**, 1013 (1966).

[20] A. Van Den Bosch, J. Dresselaers, J. Vansummeren, and M. Hovi, Phys. Status Solidi **11**, 479 (1972).

[21] O. D. Slagle and H. A. McKinstry, J. Appl. Phys. **38**, 446 (1967).

[22] A. V. Karlsson, Phys. Rev. B **2**, 3332 (1970).

[23] B. Nagaiah and D. B. Sirdeshmukh, Ind. J. Pure Appl. Phys. **18**, 903 (1980).

[24] Y. V. G. S. Murti and V. Usha, Physica B+C **83B**, 275 (1976).

[25] S. S. Jaswal and T. P. Sharma, J. Phys. Chem. Solids **34**, 509 (1973).

[26] R. A. Swalin, *Thermodynamics of Solids* (Wiley, New York, 1962). See also C. H. P. Lupis, *Chemical Thermodynamics of Materials* (North-Holland, Amsterdam, 1983).

[27] C. Zener, *Thermodynamics in Physical Metallurgy* (American Society for Metals, Cleveland, 1950).

[28] O. J. Kleppa, in *Metallic Solid Solutions,* edited by J. Friedel and A. Guinier (Benjamin, New York, 1963).

[29] N. B. Chanh, J. Chim. Phys. **61**, 1428 (1964).

[30] A. N. Goland, in *Atomic Structure and Mechanical Properties of Metals,* Proceedings of the International School of Physics "Enrico Fermi," Course LXI, edited by G. Caglioti (North-Holland, Amsterdam, 1976).

[31] Even in pure compounds it is known that the crystalline environment changes the free ion polarizabilities. See G. D. Mahan, Phys. Rev. B **34**, 4235 (1986); A. R. Ruffa, Phys. Rev. **130**, 1412 (1963). In a model for a solid solution, one must allow for possibly significant local fluctuations in the environment. If ion sizes were dependent on the environment, then in a solid solution, the short-range forces will have a nontrivial dependence on composition. Thus the interdependence of dielectric behavior and ionic interactions becomes more significant in solid solutions.

[32] A. R. Ubbelohde, *Melting and Crystal Structure* (Clarendon, Oxford, 1965).

[33] Simple models have been put forward to obtain vacancy formation energies in solid solutions of metals. See S. M. Kim, Phys. Rev. B **30**, 4829 (1984) and references therein. The results seem to suggest a lowering of g_f.

[34] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Dover, New York, 1964).

[35] W. T. Barrett and W. E. Wallace, J. Amer. Chem. Soc. **76**, 370 (1954).

[36] Yu. G. Vlasov and L. L. Makarov, Russ. J. Phys. Chem. **41**, 165 (1967).

[37] J. A. Wasastjerna, Soc. Sci. Fenn. Commun. Phys. Maths. XV **3**, 1 (1949).

[38] S. Chandra and J. Rolfe, Can. J. Phys. **51**, 236 (1973).