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Thermodynamics and structure of liquid binary alloys calculated using an analytic pair potential

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Analytic pair potentials proposed by Pettifor and Ward are developed using the Heine-Abarenkov pseudopotential for Li-Na, Na-K, and Na-Cs liquid binary alloys. The corresponding partial structure factors are calculated using the random-phase approximation. The calculated thermodynamic and structural properties using this real-space formalism are in good agreement with experiments.

I. INTRODUCTION

Pettifor and Ward[1] (PW) derived an analytic expression for interatomic pair potentials by replacing the Linhard free-electron gas response function with a rational polynomial. This led to an expression in the form of a sum of exponentially damped oscillatory terms and it is shown that three terms are sufficient to explain the structural phase transitions of crystalline Na, Mg, and Al under pressure. This work was later extended to liquid metals.[2,3]

In this work, we extend the formalism to liquid binary metal alloys and show that the real-space formalism we use by employing analytic pair potentials, whose parameters are calculated for each case separately by using the appropriate electron concentration and electron-ion interaction potential, is adequate to explain the observed thermodynamical properties of and concentration fluctuations in liquid binary alloys Li-Na, Na-K, and Na-Cs. We also calculate the resistivity values using the parameters thus determined.

II. PAIR POTENTIALS

The effective interatomic pair potential is given by

$$\phi_{ij}(R)=\frac{Z_iZ_je^2}{R}+\frac{1}{(2\pi)^2}\int\frac{q^2}{4\pi e^2}\left[\frac{1}{\varepsilon(q)}-1\right]v_i(q)v_j(q)e^{i\mathbf{q}\cdot\mathbf{R}}d^3q\ , \tag{1}$$

where $v_i(q)$ is the bare electron-ion potential and $\varepsilon(q)$ is the dielectric function. PW use an analytical fit to the dielectric function in the form

$$\varepsilon^{-1}(q)=\sum_m\frac{D_mq^2}{(q^2-q_m^2)}\ , \tag{2}$$

which yields,[4]

$$\phi_{ij}(R)=\frac{2Z_iZ_j}{R}\sum_m A_m\cos(k_mR+\alpha_m)e^{-\kappa_mR}\ , \tag{3}$$

where

$$A_m=2d_m|M_i(q_m)||M_j(q_m)|\ , \tag{4}$$

$$\alpha_m=\delta_m+\arg|M_i(q_m)|+\arg|M_j(q_m)|\ . \tag{5}$$

The parameters in Eq. (2) are related to the poles q_m and the weight D_m as,

$$D_m=d_m\exp(i\delta_m)\ , \tag{6}$$

$$q_m=k_m+i\kappa_m\ . \tag{7}$$

Note that D_m and q_m depend only on the density of the free-electron gas representative of the alloy, while A_m and α_m depend also on the pseudopotential used. In Eqs. (2)–(5), $M_i(q)$ is a normalized bare electron-ion interaction given by

$$v_i(q)=-\frac{4\pi Ze^2}{\Omega_iq^2}M_i(q) \tag{8}$$

with $\Omega_i=$ atomic volume of an atom of type i, which is related to the electron-density parameter r_{si} by $\Omega_i=Z_i(4\pi/3)r_{si}^3$ and

$$M_i(q)=(1-A_i)\cos qR_{M_i}+\frac{A_i}{qR_{M_i}}\sin qR_{M_i} \tag{9}$$

for the local Heine-Abarenkov potential (LHA),

$$v(R)=\begin{cases}-Ze^2A/R_M, & R<R_M\\ -Ze^2/R, & R\geq R_M.\end{cases} \tag{10}$$

The "ordering potential"

$$\phi_{\mathrm{CC}}(R)=\phi_{11}(R)-2\phi_{12}(R)+\phi_{22}(R)\ , \tag{11}$$

controls a concentration correlation function

$$g_{\mathrm{CC}}(R)=c_1^2c_2^2(g_{11}(R)-2g_{12}(R)+g_{22}(R))\ . \tag{12}$$

The corresponding concentration-concentration structure factor is defined by

$$S_{\mathrm{CC}}(q)=c_1^2c_2^2+\rho\int g_{\mathrm{CC}}(R)e^{i\mathbf{q}\cdot\mathbf{R}}d^3R\ , \tag{13}$$

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TABLE I. Input parameters.

	$Li_{0.61}Na_{0.39}$	$Na_{0.5}K_{0.5}$	$Na_{0.8}Cs_{0.2}$
r_{s1} (a.u.)	3.310[a]	4.048[d]	4.053[e]
r_{s2} (a.u.)	4.054[a]	5.037[d]	5.837[e]
R_{M1} (a.u.)	3.770[b]	3.400[c]	3.400[c]
R_{M2} (a.u.)	3.400[c]	4.200[c]	4.800[c]
A_1	1.313[b]	1.152[b]	1.120[b]
A_2	1.099[b]	1.078[b]	1.100[b]
T (K)	590	373	383

[a] Reference 8.

[b] A, R_M values for Li and other A values for metals are deduced from the fitting of the LHA model potential; Refs. 9 and 10.

[c] Reference 10.

[d] Reference 11.

[e] Reference 12.

where $c_1=c$ and $c_2=1-c$ are the atomic concentrations. In this work, we calculate $S_{ij}(q)$ Ashcroft-Langreth partial structure factors by using the random-phase approximation[5]

$$c_{ij}(R)=c_{ij}^{\mathrm{HS}}(R)-\frac{\phi_{ij}(R)}{k_B T} , \tag{14}$$

where $c_{ij}^{\mathrm{HS}}(R)$ is the hard-sphere direct correlation function in the Percus-Yevick approximation[6] and our analytic pair potentials $\phi_{ij}(R)$. The concentration fluctuations have been obtained using the long-wavelength limit[7]

$$S_{CC}(0)=c_1c_2\lim_{q\to 0}[c_2S_{11}(q)+c_1S_{22}(q) -2(c_1c_2)^{1/2}S_{12}(q)] , \tag{15}$$

where

$$S_{11}(q)=[1-\rho_2\tilde{C}_{22}(q)]/D(q) , \tag{16}$$

$$S_{22}(q)=[1-\rho_1\tilde{C}_{11}(q)]/D(q) , \tag{17}$$

$$S_{12}(q)=(\rho_1\rho_2)^{1/2}\tilde{C}_{12}(q)/D(q) , \tag{18}$$

$$D(q)=[1-\rho_1\tilde{C}_{11}(q)][1-\rho_2\tilde{C}_{22}(q)]-\rho_1\rho_2\tilde{C}_{12}^2(q) , \tag{19}$$

and $\rho_i=c_i\rho_0$ is the partial number density, $\rho_0=N/\Omega$ is the average ion density, which is related to the alloy electron-density parameter r_s by $\Omega=Z(4\pi/3)r_s^3$.

TABLE II. Calculated pair-potential parameters.

Alloys	n	$k_n/2k_f$	$\kappa_n/2k_f$	A_n	α_n/π
	1	0.257	0.769	1.877	−0.164
$Li_{0.61}Na_{0.39}$	2	0.618	0.530	1.313	−2.375
	3	0.804	0.225	0.025	−0.342
	1	0.306	0.916	2.081	−0.338
$Na_{0.5}K_{0.5}$	2	0.736	0.632	0.671	−0.801
	3	0.959	0.269	0.016	−0.865
	1	0.306	0.915	2.151	−0.351
$Na_{0.8}Cs_{0.2}$	2	0.735	0.632	0.633	−0.815
	3	0.959	0.269	0.015	−0.849

TABLE III. Calculated internal energies, pressures, and bulk moduli.

Alloys	$-U$ (Ryd)	$-P$ (10^{10} dyn/cm^2)	B (10^{10} dyn/cm^2)
$Li_{0.61}Na_{0.39}$	0.449	1.444	4.957
$Na_{0.5}K_{0.5}$	0.432	1.564	2.320
$Na_{0.8}Cs_{0.2}$	0.626	1.533	4.409

III. THERMODYNAMIC PROPERTIES

The total internal energy u per ion is given by

$$u=\frac{3}{2}k_BT+u(n_0) +2\pi\rho_0\sum_{i,j}c_ic_j\int_0^\infty R^2\phi_{ij}(R)g_{ij}(R)dR , \tag{20}$$

where $n_0=NZ/\Omega$ is the average conduction-electron density for the alloy and

$$u(n_0)=Zu_{eg}+\frac{1}{2}Z\Omega^2\frac{d^2u_{eg}}{d\Omega^2}+\frac{1}{2}\sum_i\phi_{ii}^{bs}\ (R=0) . \tag{21}$$

The pressure and bulk modulus can be obtained from this expression by taking appropriate derivatives. The advantage of this real-space formalism is that the total energy is a sum of only two terms, one of which contains all the structure-dependent contributions. The main contribution to the total energy is from the $\phi(R=0)$ term.

IV. RESULT AND CONCLUSIONS

The input electron densities determined from experiments and LHA potential parameters listed by other

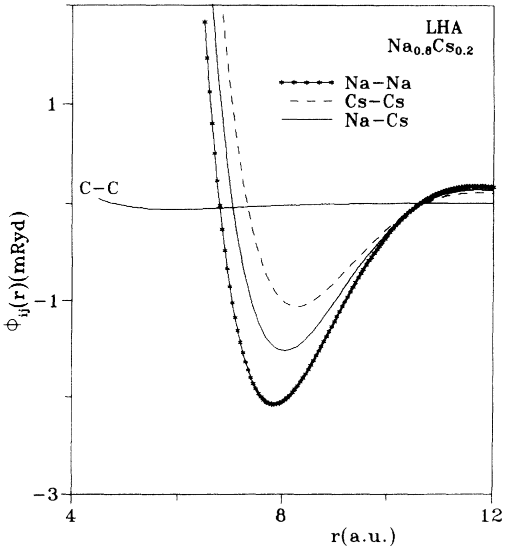

FIG. 1. The ordering and pair potentials for Na-Cs.

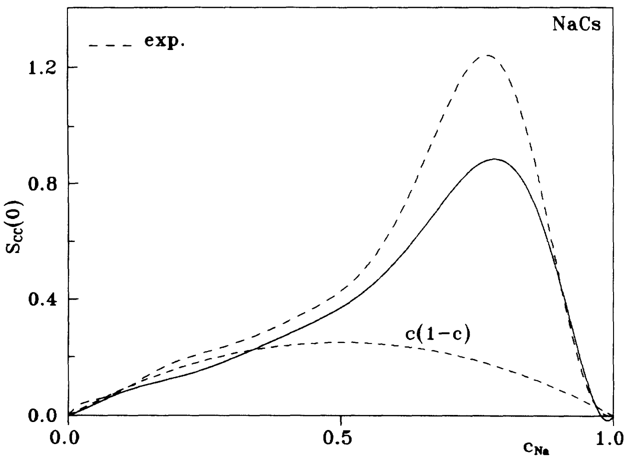

FIG. 2. The limiting values $S_{CC}(0)$ for concentration-concentration structure factor of Na-Cs.

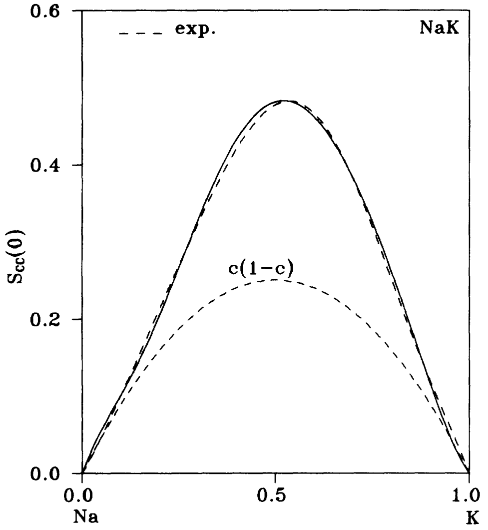

FIG. 3. The limiting values $S_{CC}(0)$ for concentration-concentration structure factor of Na-K.

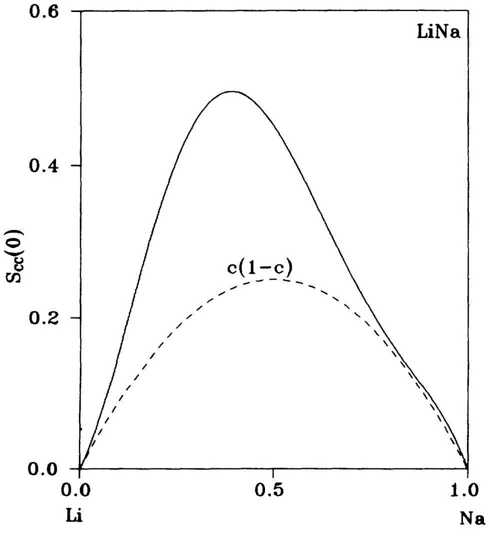

FIG. 4. The limiting values $S_{CC}(0)$ for concentration-concentration structure factor of Li-Na.

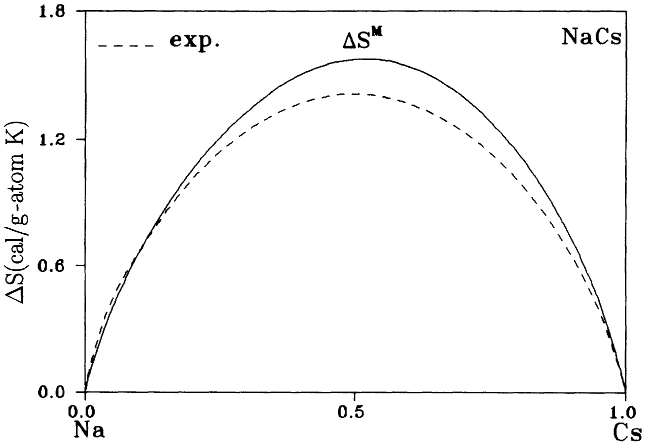

FIG. 5. The entropy of mixing ΔS^M for Na-Cs.

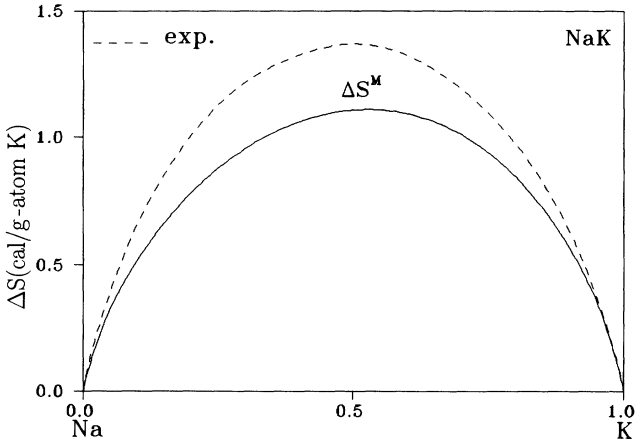

FIG. 6. The entropy of mixing ΔS^M for Na-K.

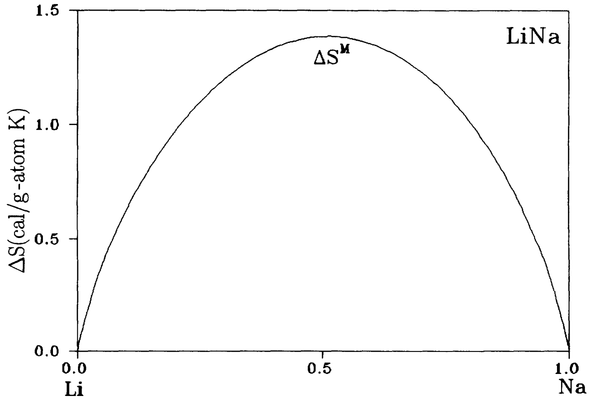

FIG. 7. The entropy of mixing ΔS^M for Li-Na.

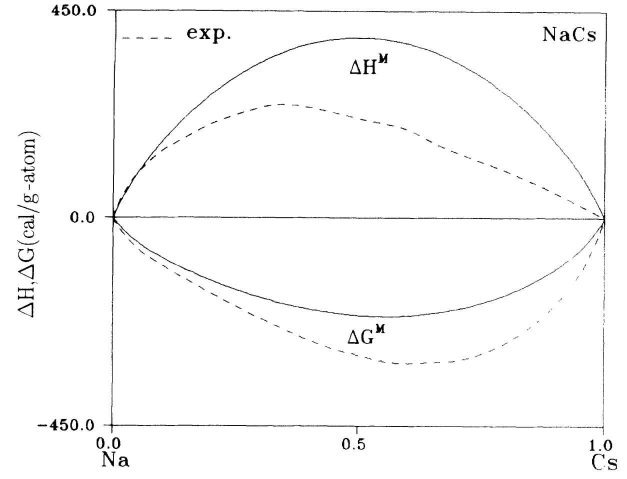

FIG. 8. The enthalpy of mixing ΔH^M and free energy of mixing ΔG^M for Na-Cs.

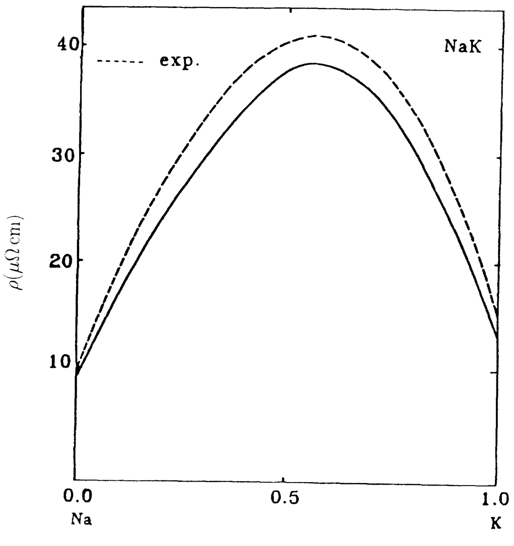

FIG. 11. The Faber-Ziman resistivity values for Na-K.

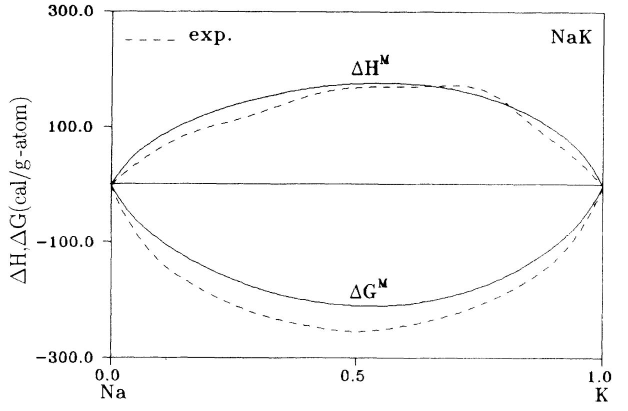

FIG. 9. The enthalpy of mixing ΔH^M and free energy of mixing ΔG^M for Na-K.

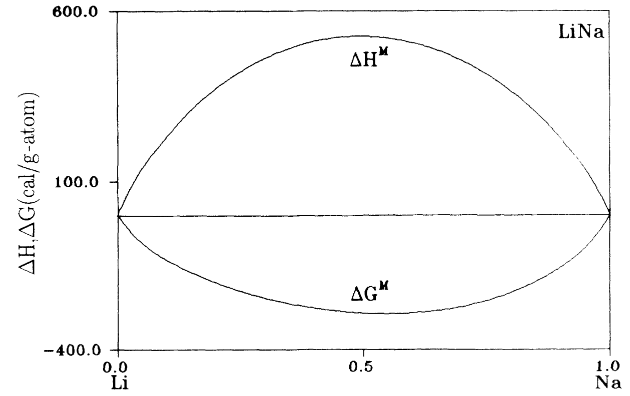

FIG. 10. The enthalpy of mixing ΔH^M and free energy of mixing ΔG^M for Li-Na.

workers are given in Table I.[8–12] All reported values are for critical alloy concentrations.

The calculated pair-potential parameters using only these input values are given in Table II. The pair potentials calculated using these parameters are shown in Fig. 1, for Na-Cs as an illustrative case. Also shown in the same figure is the ordering potential $\phi_{CC}(R)$, which is negative in the nearest-neighbor distance showing a phase separating tendency. We find the same behavior also in the cases of Na-K and Li-Na, as expected.

The calculated $S_{CC}(0)$ values are shown in Figs. 2–4 for $Na_{0.8}Cs_{0.2}$, $Na_{0.5}K_{0.5}$, and $Li_{0.61}Na_{0.39}$, respectively, and are compared with experimental values[12–14] in cases where the experimental information is available. The observed deviation from the ideal behavior and overall agreement with experiment is satisfying.

The calculated internal energy, pressure, and bulk modulus values, using the input values listed in Table I, are given in Table III. Electron densities of alloys are taken from experiments.

Although, the bulk modulus values are not available for the same concentrations, they can be compared with equiatomic concentration values of 2×10^{10} dyn/cm^2, 3.3×10^{10} dyn/cm^2 for Na-Cs, Na-K, respectively.[15,16]

We also calculated other thermodynamic functions such as entropy, enthalpy, and free energy of mixing. These are given in Figs. 5–10 and compared with available experimental values.[12,13,17] The agreement with experimental data is quite encouraging.

We tested our parameters further by calculating the Faber-Ziman resistivity values which are shown in Fig. 11, for Na-K as an illustrative case. The results clearly show that the present real-space approach is capable of producing good quality analytical pair potentials suitable for use in computer simulation studies.

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