

Structure and thermodynamics of liquid metals and alloys

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Ab initio calculations of the structure and the thermodynamic properties of simple liquid metals and alloys are presented. The basic ingredients of the theory are as follows: (a) An orthogonalized-plane-wave-based first-principles pseudopotential is used to describe the interatomic forces. The pseudopotential is optimized specifically for binary systems. The $X\alpha$ method is used to construct the electron-ion potential. (b) A system of hard spheres is used as a reference system for describing the liquid structure. Effective hard-sphere diameters are determined by a variational method based on the Gibbs-Bogolyubov inequality. The method of this paper yields encouraging results for the structure factors, the excess volume, and the enthalpy and entropy of formation for alloys with a nearly random distribution of the components. Difficulties arise where nonrandomness has to be expected. The theory provides a basis for a microscopic understanding of the thermodynamics of alloys of simple metals in terms of their electronic structure.

I. INTRODUCTION

The theoretical basis for an understanding of the thermodynamics of simple liquid metals has been forged in recent years to a point where it can be used to calculate thermodynamic properties with some success.¹⁻⁵ This advance has been made possible due to the combination of the pseudopotential theory with thermodynamic perturbation theories. The pseudopotential theory enables one to formulate the energy in terms of the pseudopotential and of the structure factor.⁶ On the other side it is possible to write down closed-form expressions for the thermodynamic quantities of hard-sphere systems, including the structure factor, in the Percus-Yevick approximation.⁷⁻⁹ A link between both theories is provided by a variational technique based on the Gibbs-Bogolyubov inequality.¹⁰ This inequality states that when the Hamiltonian of a given system is regarded as the Hamiltonian of a reference system plus a perturbation, the free energy of the system will always be smaller than that of the reference system plus the expectation value of the perturbation (calculated with the structure factors of the reference system). In our case, the reference system is one of hard spheres, and the hard-sphere diameters will be chosen to minimize the free energy.

The theory is readily generalized to binary-liquid systems, closed-form expressions for the thermodynamics of hard-sphere mixtures being available.¹¹⁻¹³ So far however, difficulties connected with the pseudopotential description of binary systems have prevented a widespread use of this scheme for alloy calculations. The papers of Stroud¹⁴ on the phase separation in lithium-sodium, of Umar *et al.*¹⁵ on the enthalpy and entropy of sodium-potassium, and of Stevenson¹⁶ on liquid hydrogen-helium mixtures are, to our knowledge,

the only comprehensive calculations for alloys. On the other side, the theory has been used by Umar *et al.*^{17,18} and Yokoyama *et al.*¹⁹ to parameterize the excess entropy of formation of binary alloys in terms of pseudopotential and hard-sphere parameters. It emerges from these investigations that the excess entropy of binary alloys depends very largely on the excess volume of formation. In the above-mentioned alloy calculations, the volume of formation has either been neglected¹⁵ or taken from experiment.¹⁷⁻¹⁹ Stevenson¹⁶ predicts a small negative volume of formation for hydrogen-helium mixtures.

We have recently presented an optimized first-principles pseudopotential scheme for binary alloys^{20,22} (hereafter these papers will be referred to as I and II), which is a generalization of Harrison's pure-metal theory. The approach is based on an expansion of the valence-electron states in the alloy in terms of generalized orthogonalized plane waves, the $X\alpha$ method being used to construct the electron-ion crystal potential. Generally the pseudopotential will be different in the pure metal and in an alloy due to (i) the change in the chemical potential, (ii) the change in the core-shift which is produced by the modified surrounding of the ions, and (iii) a redistribution of the electronic charge caused by changes in the orthogonalization and in the screening. All these effects are taken into account in the optimized pseudopotential scheme. The theory has been used successfully to calculate the enthalpies and volumes of formation of solid LiMg,²⁰ LiAl,²¹ and binary alkali-metal systems.²² It predicts correctly the structure and range of stability of the LiMg alloy phases and their low-temperature ordering behavior. Zintl-phase formation is predicted for LiAl. The crystal-structure parameters and the enthalpies and volumes of formation of the highly

complex alkali-metal intermetallic compounds Na_2K , Na_2Cs , K_2Cs , and K_7Cs_6 have been explained with surprisingly high accuracy. Thus it appears that the concept of pseudopotential optimization is very useful in the perturbation treatment of binary crystals.

In this paper, our optimized pseudopotentials are used in the variational thermodynamic perturbation scheme to determine appropriate effective hard-core diameters for seven simple metals and their alloys. The calculated diameters are very realistic in each case and produce structure factors which agree reasonably well with recent measurements. For all the pure metals, the calculated excess entropies are in a very good agreement with experiment. Departures of the interionic potential from the hard-sphere behavior show up in the calculation of derived thermodynamic quantities: the isothermal bulk modulus, the thermal expansion coefficient and the heat capacities at constant pressure and volume are calculated with very good accuracy for aluminium, magnesium and lithium, but with a lower accuracy for the heavier alkalis, as the softness of the pair potential increases.

The variationally determined hard-sphere diameters change substantially in the alloy. The change in the hard-sphere diameter may be traced back, via the effective interionic pair potentials, to changes in the mean valence-electron density on alloying and to a redistribution of valence electrons due to screening and orthogonalization.

No experimental information is available on the partial structure factors of binary alloys of simple metals. In order to make at least a global comparison with experiment, we use our theoretical partial structure factors to calculate the x-ray scattering intensity for sodium-potassium and aluminium-magnesium alloys and neutron-scattering intensity for sodium-potassium.

The calculated enthalpies of formation are the result of a close cancellation between free-electron, band-structure, and electrostatic contributions. Their reasonable agreement with experiment is taken to constitute a stringent test of our theory. The experimentally known formation volumes are also well reproduced. Again the trends in the volume change on alloying may be interpreted in terms of the interionic potentials. Difficulties are encountered in describing the lithium-magnesium and lithium-aluminum alloys, where the experimentally well-known "chemical compression" of the lithium ion is overestimated (cf. e.g., Ruppertsberg and Speicher).²³ The entropies of formation are found to be sensitive to the volume of formation. This corroborates the more empirical analysis of Umar *et al.*^{17,18}

We present a systematic study of the change of

the bulk modulus, the thermal expansion coefficient, and the specific heat on alloying. The final section is devoted to a discussion of our results.

II. OPTIMIZED PSEUDOPOTENTIALS FOR BINARY ALLOYS

The pseudopotential theory presented in I is based on an expansion of the valence-electron states in the AB alloy in terms of generalized orthogonalized plane waves (OPWs). An OPW is constructed by projecting a plane wave on the subspace orthogonal to the core states ψ_{nl}^A and ψ_{nl}^B . Inserting this expansion in the one-particle Schrödinger equation, one obtains a generalized Phillips-Kleinman equation for the pseudo-wave-function. Within this general class of pseudopotentials, an optimized pseudopotential may be selected using Cohen and Heine's criterion²⁴ of the smoothest pseudo-wave function. The resulting electron-ion pseudopotential may again be factorized in terms of form factors w_A, w_B and structure factors S_A, S_B describing the spatial arrangement of the A and B ions. The form factor of the A component is given by [we use atomic units ($\hbar = 2m = e^2/2 = 1$) in our pseudopotential calculations, the final results however are converted to the appropriate conventional units]

$$\langle \vec{k} + \vec{q} | w_A^0 | \vec{k} \rangle = u_A(q) + \sum_{nl} (k^2 + \langle \vec{k} | W^0 | \vec{k} \rangle - E_{nl}^A) \times \langle \vec{k} + \vec{q} | \psi_{nl}^A \rangle \langle \psi_{nl}^A | \vec{k} \rangle, \quad (1a)$$

$$\langle \vec{k} | W^0 | \vec{k} \rangle = (1 - c) \langle \vec{k} | w_A^0 | \vec{k} \rangle + c \langle \vec{k} | w_B^0 | \vec{k} \rangle, \quad (1b)$$

$$\langle \vec{k} | w_A^0 | \vec{k} \rangle = u_A(0) + (1 - \langle \vec{k} | P | \vec{k} \rangle)^{-1} \times \sum_{nl} (k^2 + \bar{u} - E_{nl}^A) |\langle \vec{k} | \psi_{nl}^A \rangle|^2. \quad (1c)$$

c is the concentration of the B component, the E_{nl}^A are the core eigenvalues in the alloy, $u_A(q)$ is the electron-ion potential, \bar{u} is the concentration average of its $q=0$ Fourier component, P is the projection operator on the subspace spanned by the ψ_{nl}^A and ψ_{nl}^B core states. For any detail, see I. The bare electron-ion potential w^0 is made self-consistent by linearly screening it by a homogeneous electron gas of the average density;

$$\langle \vec{k} + \vec{q} | w_{A,B} | \vec{k} \rangle = \langle \vec{k} + \vec{q} | w_{A,B}^0 | \vec{k} \rangle + w_{A,B}^{scr}(q), \quad (2a)$$

$$w_{A,B}^{scr}(q) = \frac{4[1 - G(q)]}{\epsilon(q)\pi^2 q^2} \int_{|\vec{k}'| \leq k_F} \frac{\langle \vec{k} + \vec{q} | w_{A,B}^0 | \vec{k}' \rangle}{k^2 - |\vec{k} + \vec{q}|^2} d^3k, \quad (2b)$$

$$\epsilon(q) = 1 + [1 - G(q)][\epsilon^{rpa}(q) - 1]. \quad (2c)$$

We use the Vashishta-Singwi²⁵ approximation for the exchange and correlation correction function $G(q)$ to the random-phase (RPA) dielectric func-

tion. The construction of the electron-ion potentials u_A, u_B and the calculation of the core-eigenvalues E_{ni}^A, E_{ni}^B is described in detail in I and in prior publications on the pure solid metals.^{26,27}

The essential point in the present theory is that the form factor w_A is different from that of the pure metal A, even recalculated at the atomic volume and valence electron density of the alloy. This change is due to different effects: (a) The core eigenvalues in the alloy are shifted relative to the pure metals. This effect combines with a further change due to the appearance of the concentration averages of the diagonal form factors in (1a) and of the electron-ion potential in (1b). (b) The projection operator P contains core states of both kinds. This will give the nonlocal repulsive parts of the form factors a different weight. This last point is also important for a correct evaluation of the one-OPW charge density, which can be divided into a homogenous part and orthogonalization holes

centered around the ionic positions. For most purposes these may be combined with the valence charge to form effective valences Z_A^*, Z_B^* which are now given by

$$Z_{A,B}^* = Z_{A,B} + \frac{2\Omega}{(2\pi)^3} \int_{|\mathbf{k}| \leq k_F} \frac{\langle \mathbf{k} | P_{A,B} | \mathbf{k} \rangle}{1 - \langle \mathbf{k} | P | \mathbf{k} \rangle} d^3k, \quad (3)$$

with the partial projection operators P_A and P_B and $P = (1-c)P_A + cP_B$. They are again different from the pure metal.

The perturbation calculus for the total energy has been described in I, here we restate only the most important results. The total energy E is given by three different contributions:

$$E = E_{fe} + E_{bs} + E_{es}. \quad (4)$$

The free-electron energy E_{fe} contains essentially the zeroth and first-order terms and depends only on the atomic volume, but not on the structure;

$$E_{fe} = \frac{3}{5} Z k_F^2 + Z E_{xc} + Z^*(V^b + V^{ex}) + f_A(1-c) \frac{2\Omega}{(2\pi)^3} \int_{|\mathbf{k}| \leq k_F} \sum_{ni} (k^2 + |\epsilon_{ni}^A| - \frac{1}{2} V_A^{opw}) \frac{|\langle \mathbf{k} | \psi_{ni}^A \rangle|^2}{1 - \langle \mathbf{k} | P | \mathbf{k} \rangle} d^3k \\ + f_B c \frac{2\Omega}{(2\pi)^3} \int_{|\mathbf{k}| \leq k_F} \sum_{ni} (k^2 + |\epsilon_{ni}^B| - \frac{1}{2} V_B^{opw}) \frac{|\langle \mathbf{k} | \psi_{ni}^B \rangle|^2}{1 - \langle \mathbf{k} | P | \mathbf{k} \rangle} d^3k. \quad (5)$$

The first and second term are the kinetic and the exchange and correlation energy of the free-electron gas, Z and Z^* being the average nominal and effective valences. The third term stems from the first-order contribution of the electron-ion potential, V^b and V^{ex} being the average $q=0$ Fourier components of the Coulomb-core and the valence-core exchange potentials. The fourth and fifth terms constitute the contribution from the repulsive parts of the pseudopotentials w^A and w^B ; ϵ_{ni}^A and ϵ_{ni}^B are the ionic core energies and V_A^{opw} and V_B^{opw} are the orthogonalization-hole contributions to the core shift, cf. I. These two terms are quite difficult to calculate accurately. On the other hand they have a large influence on the volume-dependent properties, especially on the zero-pressure density. Our calculations on the pure solid metals have shown that we can predict the lattice constants with a maximum error of a few percent.^{26,27} This is certainly as accurate as can be expected for a first-principles theory, but not accurate enough to allow a detailed comparison of our calculated thermodynamic quantities with experiment. Therefore, we introduced adjustable prefactors f_A and f_B in Eq. (5). They are determined by fitting the density of the pure liquid metal at the melting point. The same parameter is used to scale the corresponding contribution of each of the compo-

nents in the alloy.

The band-structure energy E_{bs} is just the effective potential energy due the indirect interaction between the ions via the conduction electrons. According to the thermodynamic variation principle stated in the introduction, one needs only the expectation value of this potential, averaged over the reference system. Consequently, E_{bs} is given by

$$E_{bs} = \sum_{i,j} \frac{\Omega}{2\pi^2} \int_0^\infty F_{ij}(q) \bar{S}_{ij}(q) q^2 dq \quad (6a)$$

$$F_{ij}(q) = \frac{2\Omega}{(2\pi)^3} \int_{|\mathbf{k}| \leq k_F} \frac{\langle \mathbf{k} + \mathbf{q} | w_i | \mathbf{k} \rangle \langle \mathbf{k} | w_j | \mathbf{k} + \mathbf{q} \rangle}{k^2 - |\mathbf{k} + \mathbf{q}|^2} d^3k \\ - \frac{q^2}{16\pi} \frac{w_i^{scr}(q) w_j^{scr}(q)}{1 - G(q)}. \quad (6b)$$

The w_i are the screened form factors and the w_i^{scr} are the screening potentials [Eqs. (1) and (2)]. There two possible choices for the partial energy wave-number characteristics F_{ij} and the partial structure factors \bar{S}_{ij} : (a) the w_i 's are the form factors of the two components, w_A and w_B ; and the \bar{S}_{ij} , $i, j = A, B$ are related to the Ashcroft-Langreth¹³ structure factors S_{ij} through $\bar{S}_{ij} = (c_i c_j)^{1/2} S_{ij}$. The characteristics F_{AA} , F_{AB} , and F_{BB} constitute an indirect ion-electron-ion interaction in q space. Fourier transforming and adding the direct

Coulomb repulsion yields effective pair potentials for the A - A , A - B , and B - B interactions. (b) The S_{ij} are the number-concentration structure factors \tilde{S}_{NN} , \tilde{S}_{NC} , and \tilde{S}_{CC} introduced by Bhatia and Thornton.²⁹ They are related in a simple way to the S_{AB} .²⁹ In this case, w_i and w_i^{scr} are the average and difference form factors \bar{w} and Δw introduced in I, F_{NN} corresponds to the \bar{F} and F_{CC} to the ΔF of that paper. S_{NN} and S_{CC} correspond to the thermodynamic averages $\langle S^*S \rangle$ and $\langle D^*D \rangle$ for a hard-sphere mixture. Hence this formalism corresponds exactly to the one used to describe random solid alloys.

The electrostatic energy E_{es} of point ions with effective valences Z_A^* and Z_B^* , immersed in a homogeneous compensating background is given by

$$E_{es} = (1-c)^2 Z_A^{*2} g_{AA} + 2c(1-c) Z_A^* Z_B^* g_{AB} + c^2 Z_B^{*2} g_{BB}. \quad (7)$$

The coefficients g_{ij} are determined by

$$g_{ij} = \frac{2}{\pi} \int_0^\infty [S_{ij}(q) - \delta_{ij}] dq, \quad i, j = A, B. \quad (8)$$

An analytic expression for g of a simple hard-sphere fluid has been given by Jones.³ This result has been generalized to a binary mixture by Ross and Seale²⁸ and by Umar *et al.*¹⁵

E_{te} , E_{bs} , and E_{es} together represent the volume and structure dependent contributions to the internal energy of a binary alloy, averaged over a reference system of a mixture of hard spheres. At a given temperature T and pressure p , it is the minimum in the free enthalpy G which determines the stable phase. This means that at a given finite temperature we have to calculate the free energy F as a function of the atomic volume and determine the equilibrium ($p=0$) values of the free energy and volume. The enthalpy difference at zero pressure is given by the difference in the equilibrium free energies.

In the thermodynamic perturbation scheme, the entropy part of the free energy is calculated in the Percus-Yevick hard-sphere approximation. Due to the two-component nature of metallic liquids there is an additional contribution from the electrons. In the noninteracting electron-gas model, the electronic contribution to the entropy is given by $S_{eg} = Z\gamma_0 T$, where $\gamma_0 = \frac{1}{2}(\pi^2 k_B^2 / k_F^2)$ is the Sommerfeld constant for the electronic specific heat. In the foregoing discussion we have implicitly assumed the valence electrons to be completely degenerate, i.e., we have approximated the Fermi distribution function by a step function. Calculating E_{te} and E_{bs} with the true distribution function would yield first- and second-order corrections to γ_0 , at the expense of considerable numerical complications, however. Further corrections arise in

principle from exchange and correlation. For the metals and alloys of interest, however, the temperatures are high enough that the electronic contribution to the entropy is small relative to the ionic contribution (generally 0.5–1.5% of the total entropy) and yet low enough to justify approximating the Fermi distribution by a step function ($E_F / k_B T$ ranges between 60 and 120). Altogether this means that within the present context, the assumption of complete degeneracy and the use of the Sommerfeld value for γ_0 are adequate.

III. HARD-SPHERE DESCRIPTION AND THERMODYNAMIC VARIATION PRINCIPLE

From the solution of the Percus-Yevick integral equation for the radial distribution functions of a hard-sphere fluid^{7,8} or a mixture of hard spheres,¹¹ there are two routes to an equation of state: The first is the compressibility (or Ornstein-Zernike) equation derived from fluctuations in the grand canonical ensemble. The second is the virial theorem relating directly the radial distribution functions and the pressure. From exact radial distribution functions, both ways will yield the same equation of state. This will not be true in general, if distribution functions derived from an approximate theory such as the Percus-Yevick equation are used. Carnahan and Starling⁹ showed that for a pure hard-sphere fluid a better equation of state results by averaging the pressures derived from the compressibility and from the virial equations in the ratio 2:1. Mansoori *et al.*¹² generalized this approach to the two Percus-Yevick equations of state derived by Lebowitz and Rowlinson³¹ for hard-sphere mixtures. The three variants of the equation of state will be labelled C , V , and CS , respectively.

Consider a binary mixture of $(1-c)N$ hard spheres with diameter σ_A and cN with diameter σ_B . The free energy may be expressed in terms of the packing fraction η (i.e., the volume occupied by the hard spheres divided by the total volume) and of the hard-sphere diameters in the following way:

$$F_{hs} = \frac{3}{2} k_B T - TS_{hs}. \quad (9)$$

The first term is the internal energy of an ideal gas and the entropy of the hard-sphere mixture is given by

$$S_{hs} = S_{gas} + S_c + S_\eta + S_\sigma, \quad (10)$$

where S_{gas} is the ideal gas entropy, S_c is the ideal entropy of mixing, and S_η depends only on the packing density. The last term S_σ corresponds to the mismatch between the hard spheres with different radii. Closed-form expressions for all these quantities have been given by Umar *et al.*^{15,18} for the C and CS cases. The pure metal result is included

if we set $c=1$ or $c=0$, in this case $S_c = S_0 = 0$.

Equations (9) and (10) constitute the free energy of our reference system F_{hs} ; the configuration average of the total interaction potential, performed over the reference system, $\langle V \rangle_{\text{hs}}$ has been formulated in Sec. II. According to the Gibbs-Bogolyubov inequality, the sum of these terms constitutes an upper bound to the free energy of the real system:

$$F \leq F_{\text{hs}} + \langle V \rangle_{\text{hs}} \\ = \frac{3}{2}k_B T + E_{\text{te}} + E_{\text{hs}} + E_{\text{es}} - TS_{\text{hs}} - \frac{1}{2}\gamma_0 Z T^2. \quad (11)$$

Since (11) constitutes an upper bound, it follows that at a given temperature and volume, the best hard-sphere diameters and the best estimate for the free energy are given by

$$\left(\frac{\partial F}{\partial \sigma_A} \right)_{\Omega, T, \sigma_B} = \left(\frac{\partial F}{\partial \sigma_B} \right)_{\Omega, T, \sigma_A} = 0. \quad (12)$$

As a consequence of the variational condition (12), the entropy per ion is given by $S = S_{\text{hs}} - \gamma_0 Z T$.¹⁵

We want to calculate the equilibrium ($p=0$) values of the volume and of the free energy. Therefore, for each temperature, the variational procedure has to be repeated for different volumes. The equilibrium values are then determined by a simple interpolation procedure.³² This calculation yields at once the isothermal compressibility. The isobaric expansion coefficient, $\alpha = \Omega^{-1}(\partial \Omega / \partial T)_p$ may be calculated in two different ways: (a) the variational procedure is repeated at a higher temperature and the definition is treated as a difference equation. (b) Alternatively, α may be reformulated using the Maxwell relations $\alpha = \Omega^{-1}(\partial S / \partial p)_T$. This is again calculated by numerical differentiation. We anticipate that both methods should yield identical results. The specific heat at constant pressure is calculated by numerically differentiating the entropy, $C_p = T(\partial S / \partial T)_p$. The specific heat at constant volume may be calculated using $C_\Omega = T(\partial S / \partial T)_\Omega$ or using $C_\Omega = C_p - \alpha^2 \Omega B_T T$, again both methods yield results which are in good agreement. This shows that our numerical procedures are accurate enough.

IV. PURE LIQUID METALS

We have summarized the basic ingredients for the *ab initio* thermodynamic calculations for liquid metals and alloys in Secs. II and III. We turn now to specific applications of this scheme. First we present our results for the pure metals. The adjustable prefactor f in the repulsive contribution to E_{te} (Eq. 5) has been used to fit the experimental densities at the melting point, as given in Table I. f deviates only slightly from $f=1$, i.e., the corrections introduced by fitting f corresponds to a change of a few percent in the diagonal pseudopo-

tential matrix element. All three variants of the hard-sphere equation of state have been used. The calculated packing fractions, effective hard-sphere diameters and excess entropies are summarized in Table I. The excess entropy is defined as the difference between the total entropy and the ideal gas entropy, $S_E = S - S_{\text{gas}}$. It can be seen at once that the packing fractions are very realistic throughout, even for Li, where recent model-potential calculations encountered some difficulties.³⁷ In all cases, the virial equation of state leads to a distinctly higher packing density than the compressibility equation, the Carnahan-Starling equation yielding intermediate values close to the C value. Since S_η is a monotonically decreasing function of η , and $S_\eta^V > S_\eta^C > S_\eta^S$,⁵ the calculated excess entropies are nearly identical, in spite of the differences in η . For the alkali metals, the excess entropies are in excellent agreement with experiment. For the polyvalent metals aluminum and magnesium they are somewhat lower but still very reasonable.

From the calculated packing fractions, we obtain at once the static structure factors. The results of our calculations are represented in Fig. 1, together with the experimental results determined by inelastic neutron or x-ray scattering. According to the larger packing density, the V approach yields a higher main peak than the C approach, the CS peak lying in between but closer to the latter. Great care has to be exercised in selecting appropriate experimental structure factors. There has been some discussion on the reasons for the difference in the structure factors determined by neutron and x-ray scattering (see, e.g., Egelstaff *et al.*⁴⁴), which manifests itself mainly in the height of the first peak, $S(q_0)$. From the change in the x-ray scattering factors in a free atom and in a metal, one would expect $S(q_0)$ to be higher for neutron than for x-ray scattering, and long-range electronic correlations have been invoked to account for the apparently reversed experimental situation.⁴⁴ Very recent neutron experiments,^{38,40-42} however, produced much higher peaks than the early experiments of Gingrich and Heaton.⁴⁵ Compared to the modern experiments the height of the main peak is distinctly underestimated. For these metals, the oscillations for $q > q_0$ are less damped and slightly shifted to larger q , compared to the experimental $S(q)$. For the polyvalent metals Al and Mg the hard-sphere structure factor with η_C or η_{CS} reproduces the experimental $S(q)$ very well, while η_V leads to an overestimate of the first peak.

The relatively poor results for the alkali structure factors may be ascribed to the softness of the interionic pair potential and to the neglect of its attractive part. This may be illustrated by consid-

TABLE I. Atomic-volume, Ω , correction factor to the repulsive contribution to E_{te} , f , packing fraction η , effective hard-core diameter σ and excess entropy S_E . The calculations have been performed using the compressibility, the virial- and the Carnahan-Starling equations of state.

	T (°C)	Ω (a.u.)		f	η	σ (a.u.)	$-S_E/k_B$	
							Theory	Expt.
Li	180	151.25 ^a	C	0.988	0.435	5.01	3.73	3.61 ^e
			CS	0.989	0.442	5.04	3.75	3.70 ^f
			V	0.992	0.458	5.10	3.80	
Na	100	277.89 ^b	C	0.934	0.421	6.07	3.47	3.45 ^e
			CS	0.936	0.426	6.10	3.47	3.55 ^f
			V	0.942	0.440	6.16	3.50	
K	65	531.19 ^b	C	0.896	0.420	7.49	3.43	3.45 ^e
			CS	0.901	0.424	7.51	3.41	3.61 ^f
			V	0.903	0.442	7.62	3.51	
Rb	35	642.41 ^b	C	0.886	0.433	8.02	3.66	3.63 ^e
			CS	0.889	0.438	8.05	3.65	
			V	0.892	0.455	8.15	3.72	
Cs	35	851.36 ^c	C	0.899	0.430	8.86	3.59	3.56 ^e
			CS	0.900	0.436	8.90	3.60	
			V	0.904	0.453	9.02	3.76	
Mg	665	173.9 ^d	C	1.012	0.459	5.34	4.12	3.29 ^e
			CS	1.014	0.466	5.37	4.10	3.45 ^f
			V	1.020	0.483	5.43	4.17	
Al	665	127.10 ^d	C	1.026	0.463	4.83	4.21	3.52 ^e
			CS	1.027	0.468	4.85	4.18	3.60 ^f
			V	1.030	0.479	4.88	4.10	

^aRuppersberg and Speicher, Ref. 23.

^bHujben *et al.*, Ref. 33.

^cHujben *et al.*, Ref. 34.

^d*Liquid Metals Handbook*, Ref. 35.

^eHultgren *et al.*, Ref. 36.

^fFaber, Ref. 30, p. 80.

ering the interionic pair potentials for pure K and pure Cs which are depicted in Fig. 2. We note that the variational method for defining hard-core diameters is, to a surprisingly high accuracy, equivalent to the simple thermodynamic argument proposed by Ashcroft and Langreth¹³

$$V_{\text{eff}}(\sigma) - V_{\text{min}} = \frac{3}{2}k_B T. \quad (13)$$

V_{min} is the depth of the first minimum in the effective pair potential. Equation (13) means that the effective sphere diameter is given by the distance at which the difference between the pair potential and its minimum value is just equal to the average kinetic energy of a free particle. This relation holds quite generally for all metals and alloys considered here. For Al and Mg the hard-sphere potential approximates the true interionic potential quite well (Fig. 3), and this is reflected in the structure factor.

The calculated values for the internal energies, isothermal bulk moduli and thermal expansion coefficients are compiled in Table II. The internal energies compare favorably well with the experi-

mental values calculated from the ionization energies, the room-temperature sublimation energies, heat capacities and heats of fusion quoted by Gschneider.⁴⁶ The isothermal bulk modulus may be computed by double differentiation of the free energy $B_T = \Omega(\partial^2 F/\partial\Omega^2)_T$ [the method of homogeneous compression (HC)] or from the long-wavelength limit of the static structure factor $B_T = k_B T/(\Omega S(0))$ [the method of long waves (LW)]. In the second-order perturbation approach, both values will be different, and the HC value is the correct one.⁵⁰ For solid Na and K the difference is quite small ($\leq 10\%$) and $B_T^{\text{LW}} > B_T^{\text{HC}}$. The difference is greater for the heavier alkalis. It is also important for polyvalent metals where we have $B_T^{\text{HC}} < B_T^{\text{LW}}$.⁵¹ Our calculations show that the trend is the same for the liquid metals. The agreement with experiment is excellent for Li, Mg, and Al, but a bit disappointing for the heavier alkalis. The reason for this discrepancy is the same as discussed above for the structure factor. The situation is again the same for the thermal expansion: the excellent values for Mg and Al contrast with the rather poor

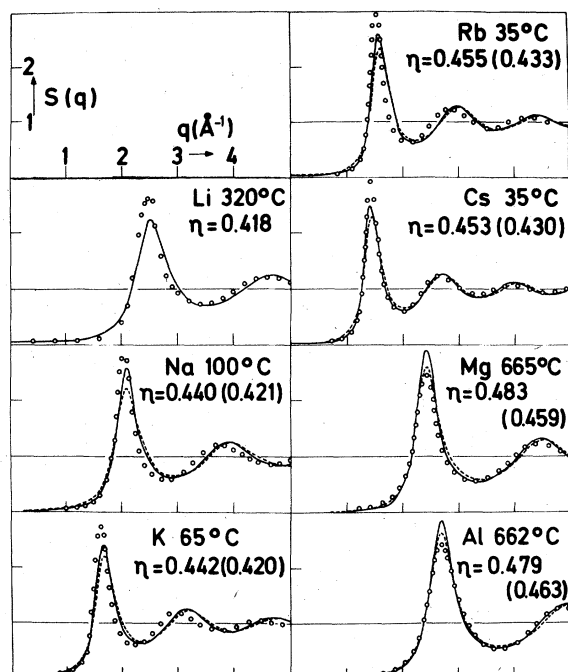


FIG. 1. Static-structure factor $S(q)$ for liquid metals, as calculated in the hard-core model using the variationally determined packing function (solid-lines V equation, broken-lines C equations, η in parentheses) and as determined by neutron (N) and x-ray (X) scattering (open circles). The experimental references are as follows: Li, Ruppertsberg and Egger (N), Ref. 38; Na, K, Greenfield, Wellendorf, and Wiser (X), Ref. 39; Rb, Copley and Rowe (N), Ref. 40; Cs, Hujben and van der Lugt (N), Ref. 41; Mg, Woerner *et al.* (X), Ref. 42; Al, Kunsch and Eder (N), Ref. 43. Except for Li, all experiments refer to temperatures very close to the melting point.

values for the alkalis. Since $\alpha = \gamma_{\Omega}/B_T$, where $\gamma_{\Omega} = (\partial p/\partial T)_{\Omega}$ is the thermal pressure coefficient, we can again ascribe the difficulties to the softness of the pair potentials.

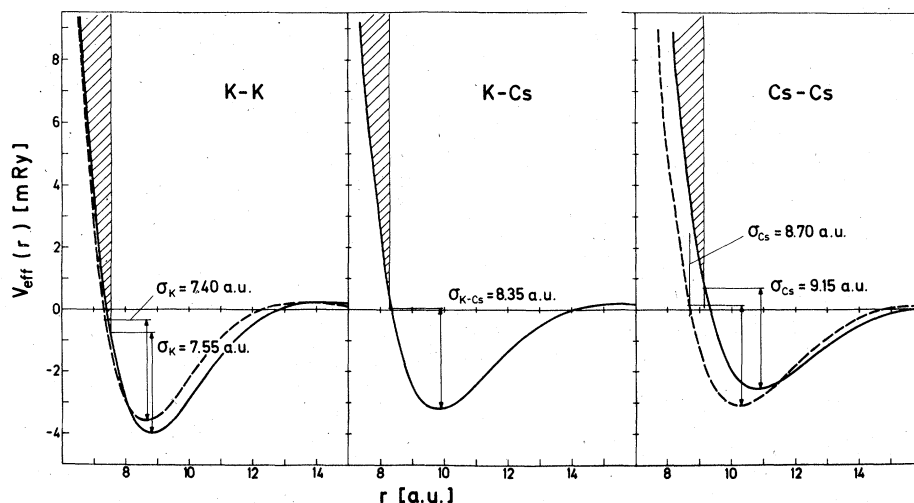


FIG. 2. Effective inter-ionic pair potentials in pure K and pure Cs (broken lines) and in an equiatomic KCs alloy at $T=200^{\circ}\text{C}$. The simple thermodynamic description for deducing effective hard-core diameters according to Eq. (13) is indicated. Note that $\sigma_{\text{KCs}} = \frac{1}{2}(\sigma_{\text{K}} + \sigma_{\text{Cs}})$ is exactly obeyed. The cross-hatched areas indicate the deviation of the repulsive part of the potentials from the hard-sphere behavior. The length of the vertical arrows corresponds to the mean kinetic energy of a free particle.

The specific heats at constant volume are predicted with fair accuracy, C_p is reproduced quite well for Al, Mg, and Li. Again the failure to produce accurate C_p 's has its origin in the soft potentials, since $C_p = C_{\Omega} + \alpha^2 B_T \Omega T$, see Table III.

We conclude that hard spheres constitute an excellent reference system for polyvalent simple metals. They are less accurate for describing the heavy alkali metals.

V. LIQUID ALLOYS

We turn now to the main point of this paper, the calculation of the thermodynamic properties of liquid alloys.

The effective hard-sphere parameters calculated using the C and CS equation are collected in Table IV. Again the packing fraction is higher in the CS than in the C approach. Compared to the pure metals both yield an increase in the packing density of approximately the same magnitude, with the exception of LiNa, however. The hard-sphere diameters change on alloying. Here we have to distinguish between two different causes: in the homovalent alkali-metal alloys, surprisingly at first glance, the diameter of the heavier (larger) ion is further increased, whereas the diameter of the smaller ion is reduced. The sum of the diameters increases very slightly (0.3–1%). Again, LiNa is an exception to this rule. The reason for the exceptional behavior of Li-containing alkali alloys lies in the strong attractive pseudopotential of Li. This leads to an accumulation of electronic charge around the Li sites, connected with an increased effective Li diameter, whereas the effective diameter of the larger ion is reduced. In the heterovalent alloys, the more electropositive ion (the one with the lower valence) shrinks, whereas the electronegative ion expands.

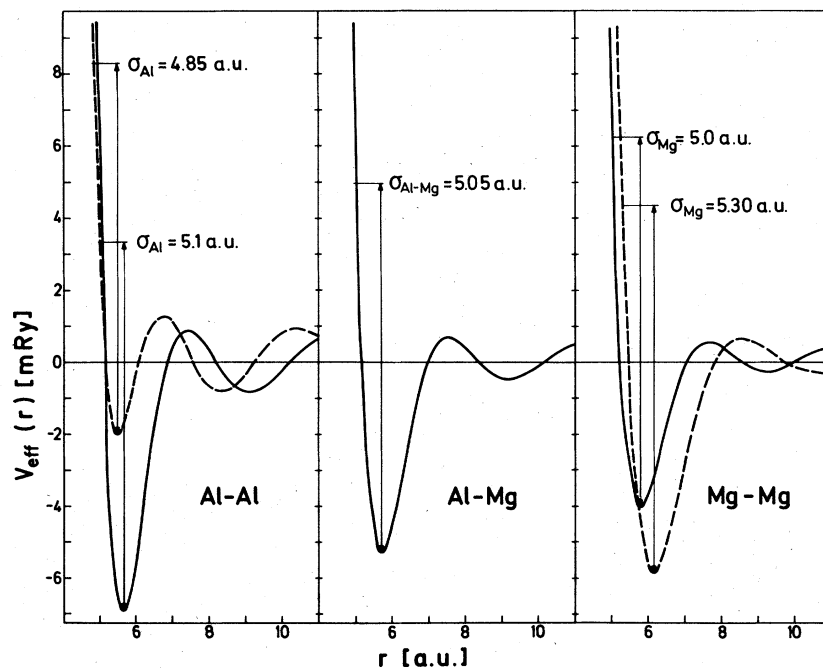


FIG. 3. Effective inter-ionic pair potentials in pure Al and pure Mg and in an equiatomic AlMg alloy. Same symbols as in Fig. 2.

The change in the hard-sphere parameters on alloying may be explained by reference to the interionic pair potentials. There are two main factors which produce a change in the effective potentials on alloying. First, there is a change in the mean valence-electron density. For homovalent alloy, this effect is equivalent to the volume effect. The volume dependence of the interionic potentials within the OPW-pseudopotential method has been discussed by the present author.⁵² Generally, the depth of the attractive first minimum is deepened when the electron density is decreased and vice versa. The first zero of the effective potential is nearly unaffected. Hence, this will leave a rela-

tively little effect on the hard-sphere diameters. More important is a kind of charge transfer due to orthogonalization effects. For solid binary alkali systems, it has been shown that this "charge transfer" is very essential in explaining the crystal structure of the intermetallic compounds. The origin of this charge transfer is as follows: if the electron density is increased around an ion, more charge will be pushed out of the core region, the orthogonalization hole charge and hence the effective valence will be increased. The effect is somewhat asymmetric, i.e., for a lower electron density, the charge transfer will change sign, but will be less pronounced. This is connected with the

TABLE II. Internal energy E , isothermal bulk modulus B_T [calculated by the methods of homogeneous compression (HC) and of long waves (LW)] and thermal expansion coefficient α .

T (°C)	E (kcal/g atom)		B_T (10^{10} dyn cm ⁻²)			α (10^{-4} K ⁻¹)		
	Theory	Expt. ^a	Theory		Expt. ^b	Theory	Expt. ^{c,d}	
			HC	LW				
Li	180	171.36	164.18	8.1	9.3	11.5	3.9	...
Na	100	149.97	145.43	3.7	3.8	5.3	5.2	2.8
K	65	127.33	122.22	1.7	1.8	2.6	6.4	2.9
Rb	35	121.82	116.68	1.3	1.5	2.0	7.8	3.4
Cs	35	110.45	108.98	0.7	1.1	1.4	10.8	3.7
Mg	665	548.82	563.55	21.6	19.7	20.4	1.71	1.66
Al	665	1292.06	1309.77	37.4	30.7	41.3	1.19	1.22

^a Calculated from the data of Gschneider (Ref. 46).

^b The values are from the compilation of Webber and Stephens (Ref. 47), except for Mg (McAlister *et al.*, Ref. 48) and Li (Ruppersberg, Ref. 38).

^c Faber, Ref. 30, p. 96.

^d Breitling and Eyring, Ref. 49.

TABLE III. Specific heat at constant pressure C_P and at constant volume C_V , and heat ratio $\kappa = C_P/C_V$. The data are for the temperatures given in Table II.

	C_P/K_B		C_V/K_B		κ	
	Theory	Expt. ^a	Theory	Expt. ^b	Theory	Expt.
Li.	4.3	3.7	3.4	...	1.3	...
Na	4.0	3.8	2.9	3.4	1.4	1.1
K	4.6	3.9	3.3	3.4	1.4	1.1
Rb	5.0	3.8	3.4	3.3	1.5	1.2
Cs	5.4	3.8	3.2	3.2	1.7	1.2
Mg	4.2	4.0	3.2	3.0	1.3	1.3
Al	3.9	3.5	3.2	2.7	1.2	1.25

^aHultgren *et al.*, Ref. 36.

^bCalculated from C_P using $C_P - C_V = \alpha^2 \Omega T B_T$ and the experimental values of α and B_T listed in Table II.

appearance of the factor $(1 - \langle \vec{k} | P | \vec{k} \rangle)^{-1}$ in the definition of the effective valence [cf. Eq. (3)]. To be concrete the effective valences in pure metals are $Z_K^* = 1.131$, $Z_{Rb}^* = 1.167$, $Z_{Cs}^* = 1.203$. In a KRb alloy they are $Z_K^* = 1.121$, $Z_{Rb}^* = 1.177$, in a KCs alloy $Z_K^* = 1.102$, $Z_{Cs}^* = 1.249$, in a RbCs alloy $Z_{Rb}^* = 1.136$, $Z_{Cs}^* = 1.222$. The consequences on the pair potentials of KCs are illustrated in Fig. 2: a bigger Z^* results in a more repulsive V_{eff} and vice versa. Thus the change in σ_A, σ_B is well explained by electronic effects.

For heterovalent alloys the relative importance of the two effects is reversed: now the change in the screening is more important. At a lower elec-

tron density, the screening electron cloud around an ion may be reduced and the potential will become more attractive. This is demonstrated in Fig. 3 at the example of Al, Mg, and their alloy.

Only very little is known of the partial structure factors of liquid alloys. From the alloys considered here, only NaK^{53,54} and AlMg⁵⁵ have been investigated by x ray and neutron scattering. The relative intensity of coherently scattered x rays may be expressed in terms of the structure factors by

$$I(q) = (1-c)f_A^2 S_{AA}(q) + cf_B^2 S_{BB}(q) + 2[c(1-c)]^{1/2} f_A f_B S_{AB}(q) = \bar{f}^2 \tilde{S}_{NN}(q) + \Delta f^2 \tilde{S}_{CC}(q) + 2\bar{f} \Delta f \tilde{S}_{NC}(q), \quad (14)$$

where f_A, f_B are the atomic scattering factors, $\bar{f} = (1-c)f_A - cf_B$, $\Delta f = f_A - f_B$ (in electronic units). We have calculated $I(q)$ for an equiatomic NaK alloy at $T = 100^\circ\text{C}$, using our hard-core parameters and the free atom scattering factors of Hanson *et al.*⁵⁶ Our result compares quite favorably with the measured intensity of Orton and Williams,⁵⁴ which is in turn corroborated by the room temperature results of Henniger *et al.*⁵³ (Fig. 4a), except for a slight shift of the first peak to smaller q 's. However, it is difficult to explain why the theoretical peak is now higher than the experimental one, since both curves are normalized to the same \bar{f} . In this connection it is interesting to con-

TABLE IV. Effective hard-sphere diameter σ_A, σ_B and packing fractions η for A - B alloys. $\Delta\eta = \eta - (\eta_A/\Omega_A + \eta_B/\Omega_B)/(1/\Omega_A + 1/\Omega_B)$ is the increase in the packing fraction on alloying.

A	B	T ($^\circ\text{C}$)		η	$\Delta\eta$	σ_A	σ_B	$\alpha = \sigma_A/\sigma_B$
						(a.u.)		
Li	Na	200	C	0.404	-0.006	5.12	5.99	0.856
			CS	0.411	-0.006	5.14	6.00	0.856
Na	K	100	C	0.431	0.015	6.06	7.57	0.800
			CS	0.435	0.017	6.04	7.62	0.792
Na	Cs	100	C	0.456	0.043	5.96	9.08	0.656
			CS	0.466	0.048	5.95	9.12	0.652
K	Rb	65	C	0.422	0.003	7.43	8.06	0.922
			CS	0.427	0.005	7.49	8.12	0.922
K	Cs	65	C	0.430	0.011	7.35	9.01	0.816
			CS	0.434	0.013	7.30	9.09	0.812
Rb	Cs	35	C	0.434	0.002	7.90	8.97	0.881
			CS	0.441	0.004	7.94	9.05	0.878
Li	Mg	700	C	0.440	0.063	4.27	5.50	0.776
			CS	0.450	0.064	4.28	5.50	0.778
Li	Al	700	C	0.481	0.088	3.68	4.97	0.740
			CS	0.503	0.103	3.70	5.01	0.740
Al	Mg	665	C	0.464	0.003	5.06	5.18	0.976
			CS	0.469	0.003	5.03	5.14	0.976

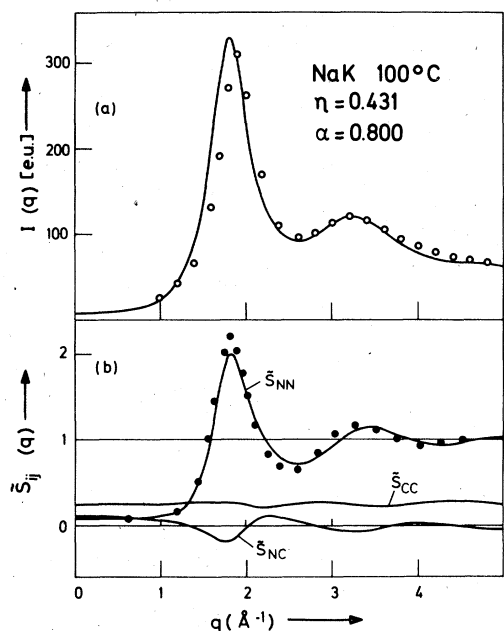


FIG. 4. X-ray scattering intensity (in electronic units) for NaK (a). Solid lines theoretical, open circles experimental (Ref. 54). Number-concentration structure factors $S_{ij}(q)$. Solid lines theoretical, full dots experimental (neutron scattering, Ref. 53).

sider the neutron results of Henniger *et al.*⁵³ Equation (20) holds for coherent neutron scattering too, with the f_A, f_B replaced the coherent scattering amplitudes, b_A, b_B . For Na and K these are practically identical: $b_{Na} = 0.351, b_K = 0.35$.⁵⁷ In this case, $I(q)/\bar{v}^2 = S_{NN}(q)$ and we obtain direct information about one of the partial structure factors. Theory and experiment are compared in Fig. 4(b), they agree very well with one another, the remaining discrepancies being the same as for pure metals. Finally, we have calculated the x-ray intensity for Al-Mg alloy at the liquidus and compared our result with the experiment of Steeb and Woerner.⁵⁵ Again the over-all agreement is very good, but the size of the first peak is overestimated when free-atom scattering factors are used. Recalculation of the scattering factors in the alloy is necessary to bring the results in line with those for the pure metal. This, however, is a subject in its own right and will be discussed elsewhere.

The zero-wave-vector limit of the partial structure factors may be calculated from thermodynamic quantities.²⁹ This calculation has been performed by McAlister and Turner⁵⁸ for NaK. They obtain $S_{NN}(0) = 0.32, S_{NC}(0) = 0.178, S_{CC}(0) = 0.402$, while our hard-core model yields $S_{NN}(0) = 0.09, S_{NC}(0) = 0.12, S_{CC}(0) = 0.24$. The small, but distinct differences indicate a deviation from an ideally random distribution and long-range fluctuations.

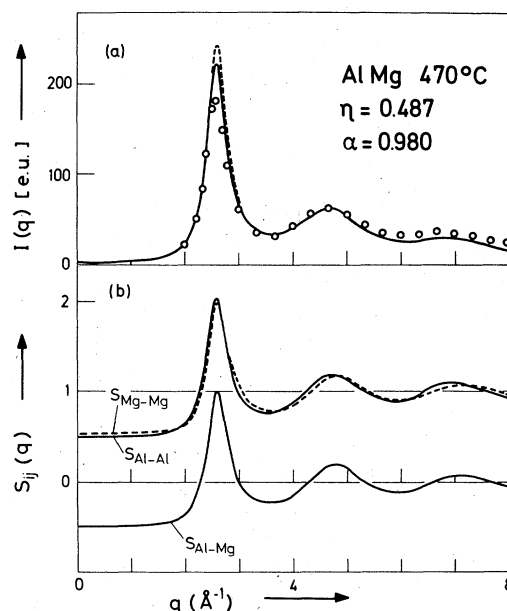


FIG. 5. (a) X-ray scattering intensity (in electronic units) for AlMg. Solid line calculated with scattering factors of Al and Mg in the alloy, broken lines calculated with free-atom structure factors. Open circles experimental results (Ref. 55). (b) Partial-structure factors.

We conclude that the hard-sphere description of partial structure factor seems to be quite reliable for larger wave vectors, but may encounter difficulties at small q .

The most stringent test for both the hard-sphere description and our pseudopotential scheme is of course the calculation of the change in volume, enthalpy, and entropy on alloying. Our results are compiled in Table V. We consider first the excess volumes. As far as experimental results are available, the agreement with our theory is as good as it can be expected to be. The large negative excess volumes of NaCs and, to a lesser extent, NaK have often been considered as puzzling, since an ideal mixing behavior seems to require $\Delta\Omega = 0$,³⁰ and there is certainly no compound formation in these liquid alloys. In II we have shown that for solid body-centered cubic solutions $\Delta\Omega/\Omega$ is very small ($< \pm 0.5\%$) for all possible combinations of two alkali metals, except Li containing phases. In the topologically close-packed intermetallic compounds on the other side, we found the change in the atomic radius Δr to be small, combined with negative excess volumes ($\Delta\Omega/\Omega = -11.6\%$ for Na_2Cs , $\Delta\Omega/\Omega = -1.3\%$ for K_2Cs , and $\Delta\Omega/\Omega = -0.8\%$ for K_7Cs_6). The last two figures indicate that the excess volume depends on the space filling of a given structure. The hard-sphere mixtures are quite densely packed, but not close packed. Again we find the change in the mean atomic radius to be

TABLE V. Volume, enthalpy, and entropy of formation for equiatomic AB alloys.

AB	T (°C)		$\Delta\Omega$ (%)		ΔH (cal/g atom)		ΔS (cal/g atom K)	
			Theory	Expt.	Theory	Expt.	Theory	Expt.
LiNa	200	C	0.25		1220		1.57	
		CS	0.40		1240		1.50	
NaK	100	C	-1.8	-1.4	470	174 ^d	1.03	1.35 ^d
		CS	-1.9		380		0.98	
NaCs	100	C	-7.1	-5.4 ^b	1870	218 ^{d,e}	0.33	1.20 ^e
		CS	-8.4		1640		0.30	
KRb	100	C	-0.16	-0.19 ^a	120	30 ^d	1.29	
		CS	-0.19		160		1.22	
KCs	100	C	-0.67		213	28 ^d	1.10	
		CS	-0.87		200		1.08	
RbCs	100	C	-1.3		-60	-32 ^d	1.13	
		CS	-1.2		-39		1.12	
LiMg	700	C	-20.3		-3410	-2477 ^d	-0.50	1.20 ± 0.6 ^d
		CS	-20.5		-3870		-0.54	
LiAl	700	C	-40.8		2450		-2.6	
		CS	-41.1		3320		-2.8	
AlMg	665	C	-4.3	-3.0 ^c	-1980	-806 ^d	1.19	1.18 ± 0.2 ^d
		CS	-4.4		-2170		1.20	

^aHujben *et al.*, Ref. 33.^bHujben *et al.*, Ref. 34.^cSteeb and Woerner, Ref. 55.^dHultgren *et al.*, Ref. 59.^eIchikawa *et al.*, Ref. 60.

small, $\Delta r/r$ ranges between 0.6% for NaCs and -0.12% for RbCs. A similar relation holds for the sum of the hard-sphere diameters: $\Delta(\sigma_A + \sigma_B)/(\sigma_A + \sigma_B)$ varies between +1.1%(NaCs) and 0.3%(RbCs). Our study suggests that for structures which allow for a favorable spatial arrangement of atoms of a different size (i.e., liquid mixtures or topologically close-packed structures), Vegard's rule should be applied to the atomic radius rather than to the volume, and this can be interpreted in terms of interionic potentials.

This interpretation holds for heterovalent alloys, too. In this case both $\Delta\Omega$ and Δr are negative, and this is correlated to a change in the hard-core diameters: $\Delta(\sigma_A + \sigma_B)/(\sigma_A + \sigma_B) = -3.3\%$ (LiMg), -9.3% (LiAl), and -0.22% (AlMg), which has been explained in terms of the screening. Our result is numerically correct for AlMg, but only qualitatively for LiMg and LiAl. In our calculation for the corresponding solid alloys we have seen the same tendency to overestimate the negative excess volume.

The calculated enthalpies of formation of the alkali alloys agree with experiment within a factor of 3. The exceptions are NaCs and KCs. No experimental values are available for LiNa, but if we repeat the calculation at elevated temperatures we find that above $T \approx 600$ °C LiNa will be miscible.

Experimentally, the phase separation occurs at $T \approx 300$ °C. Thus our ΔH and ΔS values are very realistic again. In II we have argued that s - d hybridization will contribute to the formation of intermetallic phases containing Cs and lower ΔH . This is very important for NaCs, but less important for KCs. In the alloy, the Cs ions experience an enhanced electron density, quite as in pure compressed solid Cs, where a structural phase transition connected with an electronic s - d transition is known to occur. The calculated enthalpies of formation for AlMg and LiMg are very good again. For LiAl, second-order perturbation theory is questionable. In the solid phase, covalent corrections had to be included to explain Zintl-phase formation.²¹

It is interesting to factor out the individual contributions to the enthalpy of formation. For all alkali alloys, except LiNa $\Delta E_{fe} > 0$ and ΔE_{bs} , $\Delta E_{es} < 0$. This means that the contributions favoring alloying stem from the structure-dependent pair interactions. All three contributions are seen to be volume dependent: ΔE_{es} decreases on contraction of the alloy, while ΔE_{bs} , ΔE_{fe} , and $\Delta(-TS)$ increase. This shows that the ideal-mixing behavior results from a balance between electrostatic and electronic forces.

The situation is reversed for heterovalent alloys,

now $\Delta E_{es} > 0$ and ΔE_{fo} , $\Delta E_{bs} < 0$. The volume dependence is the same as noted above. Again both the change in enthalpy and the change in the mean atomic distance is explained as a force balance. Δr has to be negative in order to lower ΔE_{es} . The decrease is counterbalanced by opposite changes in ΔE_{fo} and ΔE_{es} .

We turn now to the entropy of formation. The agreement with experiment is excellent for AlMg and quite good for NaK, though the deviation from ideality seems to be exaggerated. For KRb, KCs, and RbCs the theory predicts nearly ideal entropies of formation, so we can expect them to be very reasonable. Except for LiNa, our analysis yields an increase in the packing density, $\Delta\eta > 0$. In this case, the packing term S_η gives a negative contribution to the entropy of formation. ΔS_{gas} and ΔS_{el} are positive for homovalent alloys and negative for heterovalent alloys, but quite small in both cases. ΔS_σ is positive everywhere, but again small. Hence, the excess entropy of formation is determined mainly by ΔS_η and this depends critically on the excess volume. In our calculations, $\Delta\Omega$ is generally slightly lower than the experimental value, and this explains the trend in our ΔS . Ichikawa *et al.*⁶⁰ have shown that quite large concentration fluctuations are present in NaCs, hence a hard-sphere description becomes questionable. The failure of our ΔS calculations for LiMg and LiAl is again connected with our overestimate of the volume contraction.

Only very little is known, both experimentally and theoretically, on the change of other thermodynamic quantities on alloying. As far as experimental reference is available, our results are compiled in Table VI. For the alkali alloys, our calculations predict a decrease in the bulk modulus for nonideal systems, while for ideal systems the bulk modulus is just equal to its concentration average. This is in agreement with the experimental results. For AlMg we predict an increase of B_T on alloying, this effect is qualitatively corroborated

by experiment. For the thermal expansion coefficient we find a decrease on alloying, in agreement with experiment. Thus the assumption of a temperature-independent excess volume¹⁸ is invalid. Only for NaK specific heat measurements are available.³⁶ If extrapolated to $T = 100^\circ\text{C}$, they yield $\Delta C_p = 0$, in agreement with our result.

VI. CONCLUSION

The *ab initio* calculations of the structure and thermodynamic properties presented here are based on contributions from two different areas: (a) The pseudopotential theory is used to describe the interatomic forces in metals and alloys. (b) A system of hard spheres represents a sufficiently accurate and convenient reference system for describing the structure and the thermodynamics of metals and alloys. The Gibbs-Bogolyubov inequality provides the basis for a variational determination of effective hard-sphere diameters.

The general scheme for a hard-sphere description of binary alloys has been developed in recent years by different groups of workers,¹³⁻¹⁹ but up to now its application has been restricted to the simplest possible systems (LiNa, NaK, HHe) due to difficulties in the pseudopotential description of binary alloys. These problems can now be overcome by using an optimized first-principles theory. This theory predicts changes in the inter-atomic potentials on alloying, which can be explained in terms of screening and orthogonalization effects. Due to the orthogonalization, the effective ionic charge of the larger ions is increased on alloying, i.e., electronic charge is pushed away from the core region of the larger ion, while the orthogonalization hole of the smaller ion is reduced. This is quite similar to the "charging" effect described by Christman⁶⁴ on the basis of the augmented-plane-waves and the quantum-defect methods.

The changes in the interatomic potentials are important for both the pseudopotential and the hard-sphere contributions to the thermodynamics of al-

TABLE VI. Isothermal bulk modulus B_T and thermal expansion coefficient α for binary alloys. \bar{B}_T and $\bar{\alpha}$ are the concentration averaged quantities of the pure metals.

AB	T (°C)	B_T		\bar{B}_T		α		$\bar{\alpha}$	
		Theory	Expt.	Theory	Expt.	Theory	Expt.	Theory	Expt.
NaK	100	2.6	2.7	3.3 ^a	3.9	5.1	5.8	2.7 ^d	2.8
NaCs	100	1.7	2.2	2.0 ^b	3.4	6.0	8.0	2.8 ^d	2.9
KRb	100	1.4	1.4	2.2 ^b	2.2	6.6	7.2	2.8 ^d	3.0
AlMg	800	38.0	30.3	28.3 ^c	27.9	1.1	1.4
	1000	36.2	28.0	25.5 ^c	23.8

^aAbowitz and Gordon, Ref. 61.

^bKim and Letcher, Ref. 62.

^cMaier and Steeb, Ref. 63.

^dHujben *et al.*, Refs. 32 and 33.

loys. The calculated hard-sphere parameters for alloys reproduce the known experimental information on the structure of alloys very well. The theoretical description of the thermodynamic properties is very satisfying for LiNa, NaK, KRb, KCs, RbCs, and AlMg. Small remaining discrepancies are to be attributed to the softness of the alkali interionic potentials. Difficulties arise where either concentration fluctuations (NaCs) or short-range order effects (LiMg) may exist. A

breakdown of second-order perturbation theory seems to occur for LiAl.

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