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Heats of formation of alloys of *s-p* electronic materials

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We propose a theory of the heat of formation of alloys whose constituents are described by weak pseudopotentials. The theory gives the correct trends in the heats of formation and good, though not spectacular, quantitative results. The physical considerations on alloy formation are discussed in detail and concepts like electronegativity are clarified.

I. INTRODUCTION

The theory of pseudopotentials[1] has lead to a fundamental understanding of the nature of bonding in elemental materials with s-p electrons only in the valence bands (referred to as s-p materials hereafter). Similarly, the development of the theory of d bands[2] has yielded a great deal of insight into the structure of elemental transition metals (and compounds). Based on these developments theories of the bonding in alloys of such materials can now usefully be constructed. A possible approach in this direction is to perform detailed self-consistent one-electron calculations of ordered or disordered model compounds. Another approach is to construct simple models based on the essential physics determining the stability of alloys. Recently bonding energies of transition-metal alloys[3] and of first-row atoms to transition-metal surfaces[4] have been successfully described and understood based on tight-binding models. First-principles calculations[5] have subsequently verified the essential physical assumptions used in the former case.

In this paper, we consider the electronic binding energy of alloys of s-p materials whose electronic structure is well described by weak pseudopotentials. Heine and co-workers[6] were able to calculate the cohesive energy of such metals and metalloids by a very simple asymptotic theory to about 10% accuracy. The theory is based on model ion pseudopotentials of the form

$$V(r) = -V, \quad 0<r<R_m$$
$$= -Z/r, \quad 0<r<R_0 \tag{1}$$

where Z is the core charge of the atom, and $\Omega_0 = \frac{4}{3}\pi R_0^3$ is the average volume per atom in the solid. In the past the parameters V and R_m were obtained from spectroscopic experiments on one-electron ions. More recently it has been shown that potentials of the form Eq. (1) can yield excellent atomic spectra over a wide range of excitation energies.[7]

The bare ion potential $V(r)$, the electrostatic potential $V_{\mathrm{el}}(r)$, and the exchange and correlation potential $V_{\mathrm{xc}}(r)$ of a *uniform* charge distribution of total charge $-Z$ is averaged inside Ω_0 to get the average ($q=0$) potential, $\bar{V}$, in the solid, i.e., the bottom of a free-electron-like band. To $\bar{V}$ is added the kinetic energy of the free-electron gas and from the sum the overcounted electrostatic, exchange, and correlation energies are subtracted off to yield the total energy of the solid.

Extensions of the above theory[6] relying mainly on low-order perturbation calculations and linear-screening approximations have been used for alloys. The calculations, however, have only worked for alloys of metals with similar electronic structure, i.e., for situations close to the elemental metals themselves. There has, of course, been a great deal of other work in this field—we refer the readers to a recent symposium[8] on the subject for a comprehensive coverage of the various approaches.

We present here a new theory of alloys of s-p materials based on the pseudopotential method which also works for quite dissimilar metals. There are several difficulties in the theory of alloys of such materials which are not encountered in the theory of alloys of transition metals. For instance, while electrostatic self-consistency could be treated in a cavalier fashion during d-electron charge transfer in transition-metal alloys (the neglected s-p electrons were supposed to take care of it), it is an essential problem for s-p alloys. Related to this is the question of electronegativity differences. Consider, for instance, an alloy of Na and Al. A naive theory of the alloy focusing only on the position of the chemical potentials would predict transfer of electrons in the alloy from near Al to near Na, because E_F for Al (≈ 1.4 eV) is much higher than E_F for Na (≈ -1.7 eV), whereas chemical common sense exemplified in ideas of electronegativity suggests quite the reverse.

II. PROCEDURE

We now describe our simple asymptotic theory for s-p free-electron-like alloys. Consider two

s-p materials A and B with mean atomic volumes Ω_A, Ω_B, respectively, and with density of electronic states per unit volume $n_A(\epsilon)$ and $n_B(\epsilon)$ which are zero below the mean potentials V_A and V_B, respectively. V_A and V_B are calculated from the pseudopotential parameters as discussed above. Upon forming, for example, an equiconcentration alloy of A and B, with new total volume per atom $\tilde{\Omega}_{AB}$,[9] one may in general associate a volume $\tilde{\Omega}_A$ around A and a volume $\tilde{\Omega}_B$ around B so that $(\tilde{\Omega}_A+\tilde{\Omega}_B)/2=\tilde{\Omega}_{AB}$. Let the average local density of states per unit volume in $\tilde{\Omega}_A$ be $\tilde{n}_A(\epsilon)$ and that in $\tilde{\Omega}_B$ be $\tilde{n}_B(\epsilon)$. Let the *self-consistent* mean potentials obtained from the pseudopotential parameters and the self-consistent charge redistribution in the alloy inside $\tilde{\Omega}_A$ and $\tilde{\Omega}_B$ be $\tilde{V}_A$ and $\tilde{V}_B$, respectively. The electronic contribution to the heat of formation of the equi-concentration alloy per atom for s-p material can then be written in terms of the above quantities, by summing the one-electron energies and subtracting the multiply counted electrostatic, exchange, and correlation energies, by a slight modification of an expression derived earlier[3]:

$$\Delta E_e(AB) \approx \tfrac{1}{2} \sum_i \left(\tilde{\Omega}_i \int_{-\infty}^{\tilde{E}_F} d\epsilon\, \epsilon \tilde{n}_i(\epsilon) - \Omega_i \int_{-\infty}^{\tilde{E}_F} d\epsilon\, \epsilon n_i(\epsilon) - \tfrac{1}{2}(\tilde{V}_i - V_i)(\tilde{N}_i + N_i) \right), \quad i = A, B \tag{2}$$

where N_i is the total charge per atom i and where $\tilde{N}_i = \tilde{\Omega}_i \int_{-\infty}^{\tilde{E}_F} d\epsilon\, \tilde{n}_i(\epsilon)$ is defined as the total charge associated with atom i in the alloy. The above expression is accurate in a density functional theory including terms of $O(\Delta N_i^2)$, the only assumption being made is that within a given $\Omega_i, \tilde{\Omega}_i$ the electrostatic and exchange-correlation potentials do not vary considerably.

The key to the problem is to determine the local density of states $\tilde{n}_A(\epsilon)$ and $\tilde{n}_B(\epsilon)$. As a first approximation (to be improved on later), we consider that the lowest state lies at the self-consistent mean potential in the alloy, i.e., $\tilde{n}_A(\epsilon) = \tilde{n}_B(\epsilon) = 0$ for $\epsilon < \tilde{V}_{AB}$, where

$$\tilde{V}_{AB} = (\tilde{V}_A \tilde{\Omega}_A + \tilde{V}_B \tilde{\Omega}_B)/(\tilde{\Omega}_A + \tilde{\Omega}_B). \tag{3}$$

This amounts to assuming that the lowest state is extended and thus to neglecting any contribution from bound states due to spatial potential fluctuations. Let A have the more attractive pseudopotential, i.e., $V_A < V_B$. Then, in the alloy, states near the bottom of the spectrum will have large amplitudes in $\tilde{\Omega}_A$ and small amplitudes in $\tilde{\Omega}_B$. Correspondingly $\tilde{n}_A(\epsilon) > \tilde{n}_B(\epsilon)$ for ϵ near $\tilde{V}_{AB}$. However, for states with large kinetic energy, i.e., $(\epsilon - \tilde{V}_{AB}) \gg (\tilde{V}_A - \tilde{V}_B)$, there will be nearly equal amplitude in $\tilde{\Omega}_A$ and $\tilde{\Omega}_B$ and consistent with the assumption about the elemental materials, $\tilde{n}_A(\epsilon)$ and $\tilde{n}_B(\epsilon)$ should converge to free-electron-like behavior. From these considerations we can simply write

$$\tilde{n}_i(\epsilon) = \begin{cases} f_i(\epsilon')\epsilon'^{1/2}, & \epsilon = (\epsilon' - \tilde{V}_{AB}) > 0 \\ 0, & \epsilon' < 0 \end{cases} \tag{4}$$

with

$$f_i(\epsilon') \approx 1 \quad \text{for } \epsilon' \gg (\tilde{V}_A - \tilde{V}_B).$$

We have performed our calculations with the following form:

$$\begin{aligned} f_A(\epsilon') &= \tfrac{1}{2}(1 + 2\alpha e^{-\epsilon'/\epsilon_0})/(1 + \alpha e^{-\epsilon'/\epsilon_0}), \\ f_B(\epsilon') &= \tfrac{1}{2}/(1 + \alpha e^{-\epsilon'/\epsilon_0}), \end{aligned} \tag{5}$$

although other forms satisfying the above requirements give similar answers. In Fig. 1 we illustrate schematically the changes in the density of states described by Eqs. (4) and (5).

We now determine the parameters α, ϵ_0, and the self-consistent average alloy potential $\tilde{V}_{AB}$. The procedure we adopt is in the spirit of a self-consistent effective medium theory or coherent potential approximation.[10] Consider an isolated region $\tilde{\Omega}_A$ with mean potential $\tilde{V}_A$ embedded in the most probable configuration, i.e., in the overall mean potential of the alloy $\tilde{V}_{AB}$. Consider now the lowest state in the alloy, which by our assumption has zero energy with respect to $\tilde{V}_{AB}$. This state has a large amplitude inside $\tilde{\Omega}_A$ and by as-

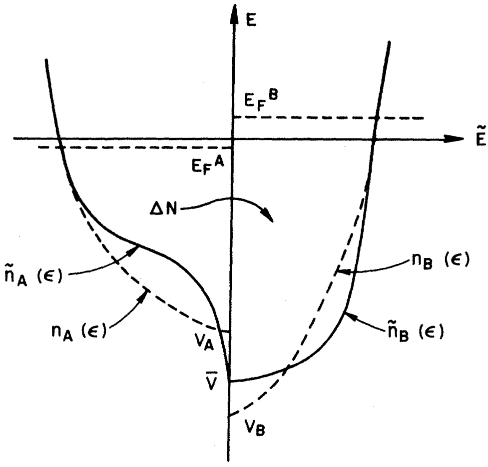

FIG. 1. Schematic illustration of the changes in the local density of states of two metals A and B upon alloying. Before alloying the mean potentials of A and B are at V_A and V_B, their local density of states are $n_A(\epsilon)$ and $n_B(\epsilon)$ with Fermi levels E_F^A and E_B^B, respectively. After alloying, as described by Eq. (2) of the text, there is a common mean potential $\bar{V}$ and a common Fermi level $\tilde{E}_F$ in the alloy, the local densities of states are $\tilde{n}_A(\epsilon)$ and $\tilde{n}_B(\epsilon)$, respectively. For the situation illustrated, B is the more electronegative element and charge is transferred from A to B upon alloying.

sumption uniform charge density associated with it outside $\tilde{\Omega}_A$. Its lowest energy in this situation requires it to be an eigenstate with energy zero for a spherical attractive potential of depth $\Delta\tilde{V}_A = \tilde{V}_{AB} - \tilde{V}_A$ inside $\tilde{\Omega}_A$. (Any state with lower energy will decay into the average medium and thus be inconsistent with our assumption of extended states.) This immediately gives the self-consistency condition

$$\Delta\tilde{V}_A(\alpha, \epsilon_0) = \pi^2/8R_A^2, \tag{6}$$

expressed in a.u. $\Delta\tilde{V}_A$ depends on α and ϵ_0 since the charge inside $\tilde{\Omega}_A$ and therefore the electrostatic, exchange, and correlation energies depend on the density-of-states parameters α and ϵ_0.

Equation (6) represents a self-consistency criterion that imposes a relationship between α and ϵ_0. Another relationship can be obtained by noting that, as in any density functional theory, we can use $n(r)$ and therefore $\tilde{N}_A/\tilde{N}_B$ as a variational parameter. This amounts to determining α for a given ϵ_0 or vice versa by minimization of the total energy of the alloy system, subject to the self-consistency constraints. Alternatively, since from physical considerations we expect ϵ_0 to be a few times $(V_A - V_B)$, we can assign it such a value and obtain α from the self-consistency considerations with very similar results.

The above procedure can be corrected perturbatively by considering spatial potential fluctuation or clustering. Let a given atom be surrounded by $(Z-1)$ other atoms in all possible ways with equal likelihood. This Z-atom cluster has the potential

$$\tilde{V}_\gamma = \frac{(Z-\gamma)\tilde{V}_A\tilde{\Omega}_A + \gamma\tilde{V}_B\tilde{\Omega}_B}{(Z-\gamma)\tilde{\Omega}_A + \gamma\tilde{\Omega}_B}, \tag{7}$$

where the configuration γ occurs with the binomial probability ${}^{Z}C_{\gamma}$. (For $Z \to \infty$, we obtain the average medium and the results discussed above.) Now we can consider local densities of states of the form of Eq. (4) for each configuration, find the Fermi level of the cluster (γ) and calculate the new energy. The new average local density of states has exponential tails from configurations that are predominantly made up of attractive A atoms. This simulates bound states and gives lowering in energy. In principle each configuration can be made self-consistent by evaluating $f_A(\gamma, \epsilon)$. We have, however, used only the $f_A(\epsilon)$ for the self-consistency of the isolated atom in the mean for all configurations. The lowering of the energy is small enough and, more importantly, without significant structure across the Periodic Table that nothing much is to be gained by making each configuration self-consistent.

III. RESULTS AND DISCUSSIONS

We have performed calculations of the heat of formation ΔH for all possible alloys formed by 16 s-p electron elements. The underlying pseudopotential parameters are taken from the tables of Animalu and Heine.[11] Even though more accurate pseudopotential parameters are available today,[8,12] the chosen potentials are known to yield cohesive energies of elemental metals[1] to within 10% which is good enough in view of the simplicity of our alloy theory. The potentials given by Animalu and Heine are nonlocal or angular momentum dependent. To simplify our task, only local averages are used in the present calculation. Several test calculations showed that the general trends in our results were unaffected by particular choices of local averages. The results presented here are all obtained by choosing the $l = 0$ pseudopotential component to represent the local average. These parameters are listed in Table I. The atomic parameters are also graphically displayed in Fig. 1 where the bottom of the valence band V, the Fermi level ϵ_F, and the crystalline atomic volume Ω are compared. We notice that for alkali metals the atomic volume increases dramatically going from Li to Cs coupled to a drastic decrease in the valence-band width. This is in contrast to the polyvalent metals where the volume increase with atomic number is rather moderate. This general difference will influence the results of alloy formation. The complete results of our alloy calculations are compiled in Table II.

To display trends in alloy stability we focus on one element, for example, Na or Si as they are combined with all chosen s-p elements. This is

TABLE I. List of pseudopotential parameters, taken from Animalu and Heine (Ref. 11). All quantities are in a.u.

	A_0	R_M	Ω	Z
Li	0.336	2.8	144.3	1
Na	0.305	3.4	254.5	1
K	0.240	4.2	481.4	1
Rb	0.224	4.4	587.9	1
Cs	0.205	4.8	745.5	1
Zn	0.99	2.2	102.0	2
Cd	0.88	2.6	144.8	2
Hg	0.97	2.6	157.8	2
Al	1.38	2.0	111.3	3
Ga	1.44	2.4	131.4	3
In	1.32	2.4	175.3	3
Tl	1.44	2.4	191.7	3
Si	2.08	2.0	134.3	4
Ge	2.10	2.0	151.8	4
Sn	1.84	2.0	181.5	4
Pb	1.92	2.1	203.4	4

TABLE II. List of heats of formation of equiconcentration alloys calculated by the method described in the paper.

	Li	Na	K	Rb	Cs	Zn	Cd	Hg	Al	Ga	In	Tl	Si	Ge	Sn	Pb
Li	0															
Na	0.2	0														
K	0.6	0.3	0													
Rb	0.7	0.3	0.0	0												
Cs	0.8	0.4	0.1	0.0	0											
Zn	0.9	1.3	1.7	1.7	1.7	0										
Cd	0.4	0.9	1.1	1.2	1.3	0.4	0									
Hg	0.3	0.7	0.9	1.0	1.2	0.5	0.4	0								
Al	0.7	0.8	1.3	1.4	1.4	0.3	0.9	0.9	0							
Ga	0.5	0.8	0.8	1.2	1.3	0.0	0.7	0.7	0.7	0						
In	0.1	0.5	0.7	0.8	0.7	0.0	0.1	0.1	0.9	0.5	0					
Si	−0.2	−0.1	0.2	0.2	0.2	−0.2	0.3	0.7	−0.1	0.4	1.0	0				
Tl	0.0	0.3	0.6	0.4	0.4	0.1	0.1	0.0	0.9	0.7	0.3	1.2	0			
Ge	−0.7	−0.1	0.0	0.0	0.0	−0.1	0.4	0.3	0.0	0.0	0.6	1.0	0.0	0		
Sn	−0.4	−0.4	−0.1	−0.4	−0.3	0.0	−0.1	0.2	0.0	0.2	0.3	0.4	0.8	0.3	0	
Pb	−0.6	−0.2	−0.2	−0.2	−0.1	0.1	−0.1	0.1	0.3	−0.1	−0.1	0.2	0.9	0.6	−0.1	0

shown in Fig. 3 (Na) and Fig. 4 (Si). All the results shown are for equiconcentration alloys. The comparison is made with the empirical parametrization of Miedema[13] for liquid alloys which is designed to give the correct sign of the heat of formation. In the Na series we find two different types of behavior. As Na is alloyed with other alkali metals, the heat of formation increases and is always positive, indicating no stable alloys. This results mainly from the drastic volume differences between Na and other alkalis and thus confirms Hume-Rothery's rule.[14] As Na is alloyed with other nonalkali elements, the heat of formation generally decreases with increasing atomic number within each column. While these trends are parallel to Miedema's results, the absolute values are too large about 0.5 eV/atom in average.

Unusually large errors (~1 eV/atom) though correct trends are found for the divalent metals Zn, Cd, and Hg. We attribute this discrepancy to the marked deviations from free-electron behavior for these metals within or near the bottom of the valence band. The second-column elements Be, Mg, Ca, Ba, and Sr could *not* be described by our asymptotic free-electron-like theory, (except for their alloys with the monovalent metals), due to the presence of strong d-like resonances[15] just above the Fermi level. The higher-valence materials (third-, fourth-, and fifth-column elements) have stronger pseudopotentials and higher Fermi levels, so that such resonances

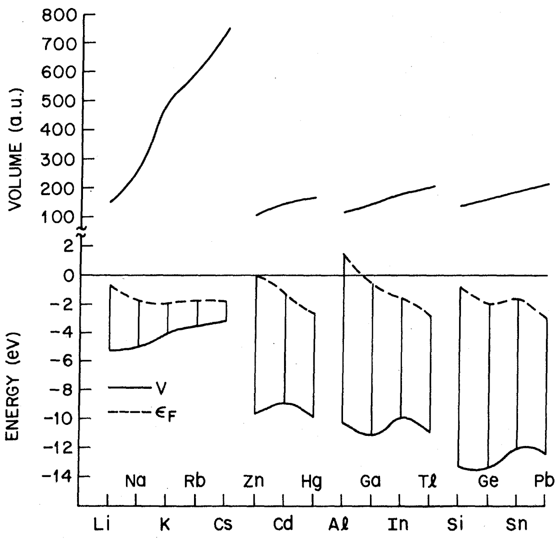

FIG. 2. Values of the principal parameters determining alloy formation for materials with weak pseudopotentials. V is the mean potential, ϵ_F the Fermi energy, and Ω the atomic volume.

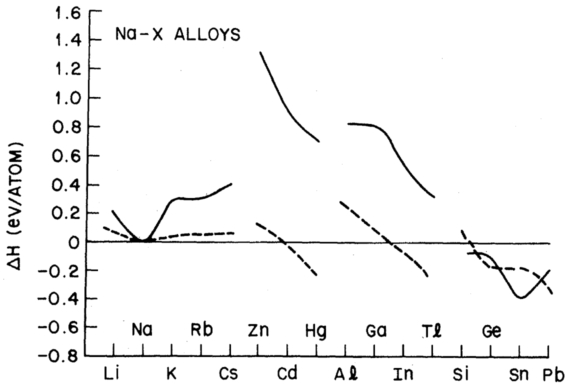

FIG. 3. Calculated heat of formation (solid curves) of equiconcentration alloys of Na with other s-p materials compared with Miedema's parametrization (dashed curves).

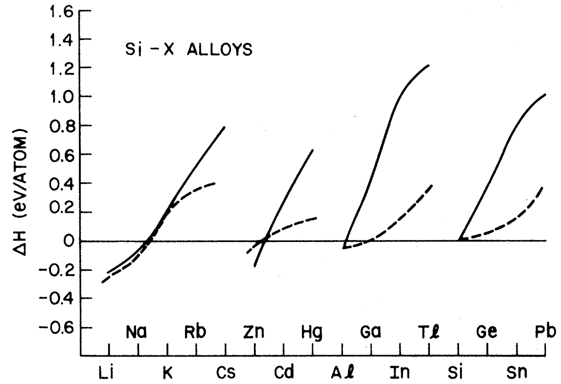

FIG. 4. Calculated heat of formation (solid curves) of equiconcentration alloys of Si with other *s-p* materials compared with Miedema's parametrization (dashed curves).

begin to be occupied giving a strong attractive contribution to the energy, a contribution not included in our theory. We thus know the limits of validity of our theory, it works when the density of states of the individual metals A and B are nearly free-electronlike not just in the occupied region of A and B separately, but also approximately in a region $|V_A - V_B|$ or $|\epsilon_{FA} - \epsilon_{FB}|$ (whichever is larger) around it.

In contrast to Na very different trends are found for Si (see Fig. 4). As Si is alloyed, the heat of formation ΔH *always* increases within each column with increasing atomic number. Generally speaking, this result can also be linked to the difference of atomic volumes.

We now analyze in some detail the various contributions to ΔH. For this purpose we consider alloys of Na with the trivalent metals Al, Ga, In, and Tl. (Similar physical points can be made with reference to the others.) In Fig. 5, we plot the variation of the "potential energy", ΔE_{pot} (this includes the electrostatic, exchange, and correlation energies plus the one-electron part), the kinetic energy ΔE_{kin}, and the perturbation cluster correction, ΔE_{pert}, against the volume difference $|\Omega_{\text{Na}} - \Omega_x|$. Note that ΔE_{pert} yields a relatively structureless lowering of ΔH across the series. This leaves the balance of ΔE_{kin} and ΔE_{pot} to determine the general trends. The kinetic energy change ΔE_{kin} is always negative and ΔE_{pot} is (generally) positive. As a function of volume difference the latter is more rapidly varying than the former and determines the trend across the series in the case shown in Fig. 5 as well as in the others. The increase in the potential energy ΔE_{pot} is simply the increase in the mean potential over that of the simple average of the two components. ΔE_{pot} is of course related to the transfer of electrons into the sphere around the more electronegative elements upon alloying.

Just precisely what makes one element more electronegative than the other is the interesting question. If no change in the local density of states LDOS was considered, charge transfer would be determined by the relative position of the Fermi level and one would get seriously wrong answers, for example, charge transfer from Al to Na. In fact, however, the local density of states is severely distorted, as illustrated in Fig. 1. For the cases considered in Fig. 5 the difference in the Fermi level of the individual metals is small and that of the mean potentials V_i is large and it is the latter which predominantly determines the distortion in the LDOS and the charge transfer. The difference in the Fermi levels does have a small effect, however. We find the charge transfer from Na to Al,

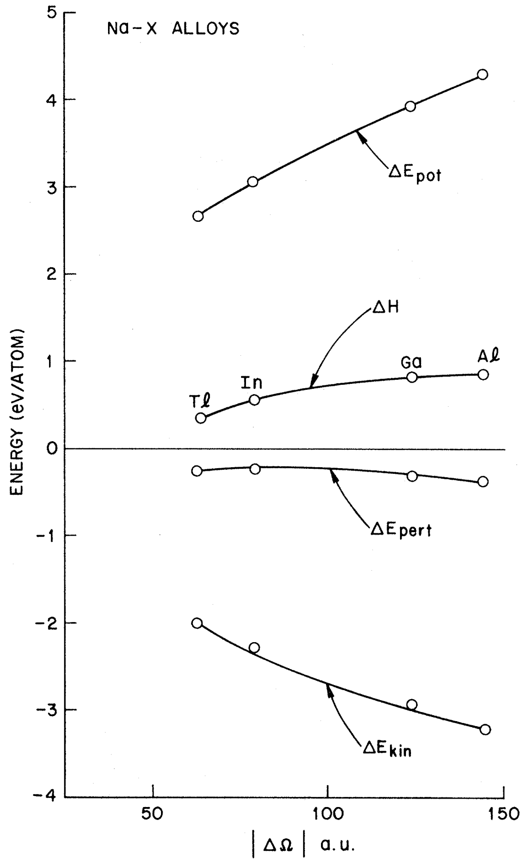

FIG. 5. Detailed consideration of contributions to the heat of formation of equiconcentration alloys of Na with trivalent metals Tl, In, Ga, and Al. It was found useful to plot the various contributions against the absolute difference in atomic volume of the constituents. ΔE_{pot} is the change in potential energy and ΔE_{kin} that of the kinetic energy. ΔE_{pert} is a small correction from considering clustering as described by Eq. (7) in the text.

Ga, In, and Tl is, respectively, 0.14, 0.20, 0.16, and $0.22e$. These numbers are best studied in conjunction with Fig. 5.

Given a certain amount of charge transfer, ΔE_{pot} is determined by the difference of one-electron potentials V_i (this is an attractive contribution to ΔE_{pot}) and the electron-electron part proportional roughly to $|(\Delta N/\Omega_A)^{1/3} - (\Delta N/\Omega_B)^{1/3}|$ which is repulsive. The latter is usually the larger contribution except when the difference of one-electron potential becomes very large, as in Na with the four-valent elements. The kinetic-energy decrease reflects directly the self-consistent change in the density of states and the requirement of a common Fermi level as illustrated in Fig. 1. The individual kinetic energy of A increases upon alloying while that of B (the more attractive element), which develops a hump in the new local density of states at low energies, decreases. This hump accomodates the extra charge transferred from A. The smaller the volume of B with respect to A, the larger is the hump [(as reflected in our calculations by the parameters α and ϵ_0 of Eq. (5)] so as to accomodate the extra charge and the greater is the decrease in kinetic energy. This trend for Na alloyed with Al, Ga, In, and Tl is illustrated in Fig. 5. We suspect that the actual local density of states of the more attractive element has a more pronounced hump than in our calculations and that we underestimate the kinetic-energy decrease. With the restriction of the form, Eqs. (4) and (5), this is the best we can do, however. There may also be a contribution towards lowering the energy from lattice relaxations which are not included in our use of Vegard's or Zen's rule[9] for the volume per element of the alloy.

There is a paucity of experimental data on the absolute magnitudes of the heats of formation. For Sn, however, a substantial amount of data is available.[16] The *heat of solution* [≈ 2 (heat of formation of equiconcentration alloys)] of Al, Cd, Ga, Ge, Li, Na, and Pb in liquid Sn is measured to be + 0.14, + 0.07, + 0.03, −0.6, and + 0.05 eV/atom, respectively. Our calculated values for the same quantity are + 0.04, −0.2, + 0.4, 0.6, −0.8, −0.6, −0.2 eV/atom, respectively. Miedema's values are + 0.14, −0.01, + .03, 0.00, −0.56, −0.31, + .07 eV/atom, respectively. It is clear, therefore, that Miedema's empiricism gives better absolute numbers than our calculations.

We have, however, demonstrated the essential physical principle involved in describing the heat of formation of alloys whose elements have weak pseudopotentials. Some confidence can also be obtained from the quantitative accuracy which is about 0.5 eV/atom while the individual cohesive energies of the elements are of the order of 10 eV.

We conclude by stating three general rules governing the heat of formation of s-p electron metals, all of which come about basically from the decrease in the local density of states at low energies of the less attractive element and an increase in the local density of states of the more attractive element.

(a) The charge transfer ΔQ occurs to the more electronegative components. The electronegativity is determined primarily by the mean potential of the components and secondarily by their Fermi levels.

(b) The charge transfer lowers the total kinetic energy and raises the total potential energy monotonicly as a function of volume.

(c) The variation in total potential energy overpowers that in total kinetic energy, thus determining the variation in heat of formation ΔH.

ACKNOWLEDGMENT

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[1] See for instance, V. Heine, M. L. Cohen, and D. Weaire, in *Solid State Physics,* edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1970), Vol. 24.

[2] See for instance, papers presented at the International Conference on Transition Metals, Toronto, 1977, published in *Transition Metals, 1977,* Conf. Ser. No. 39, edited by M. J. G. Lee, J. M. Perz, and E. Fawcett (Institute of Physics, London, 1978).

[3] C. M. Varma, Solid State Commun. 31, 295 (1979); D. G. Pettifor, Phys. Rev. Lett. 42, 846 (1979).

[4] C. M. Varma and A. J. Wilson, Phys. Rev. 22, 3795 (1980).

[5] A. R. Williams, C. D. Gelatt, Jr., and V. L. Moruzzi, Phys. Rev. Lett. 44, 429 (1980); see also R. E. Watson and L. H. Bennett, Phys. Rev. Lett. 43, 1130 (1979).

[6] See V. Heine and D. Weaire in Ref. 1.

[7] J. Starkloff and J. D. Joannopoulos, Phys. Rev. B 16, 5212 (1977).

[8] *Proceedings of the Symposium on Alloy Phase Formation, AIME, New Orleans, 1979* (in press).

[9] Simple averages as proposed by Vegard or by Zen can be used. See, e.g., W. B. Pearson, *The Crystal Chemistry and Physics of Metals and Alloys* (Wiley, New York, 1972), p. 174.

[10] For a review see H. Ehrenreich and L. M. Schwartz, in *Solid State Physics,* edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1976).

1976).

[11] A. O. E. Animalu and V. Heine, Philos. Mag. 12, 1249 (1965).

[12] D. R. Hamann, M. Schlüter and C. Chiang, Phys. Rev. Lett. 43, 1494 (1979).

[13] A. R. Miedema, Philips Tech. Rev. 36, 217 (1976); A. R. Miedema, R. Boom, and F. R. deBoer, J. Less-Common Met. 41, 263 (1975); Calphad 1, 345 (1977); for a review see A. R. Miedema, F. R. deBoer and P. F. deChatel, Physica (Utrecht) 100, 1 (1980).

[14] W. Hume-Rothery and G. V. Raynor, *The Structure of Metals and Alloys* (Institute of Metals, London, 1962).

[15] V. L. Moruzzi, J. F. Janak, and A. R. Williams, *Calculated Electronic Properties of Metals* (Pergamon, New York, 1978).

[16] R. Boom, Scr. Metall. 8, 1277 (1974).