

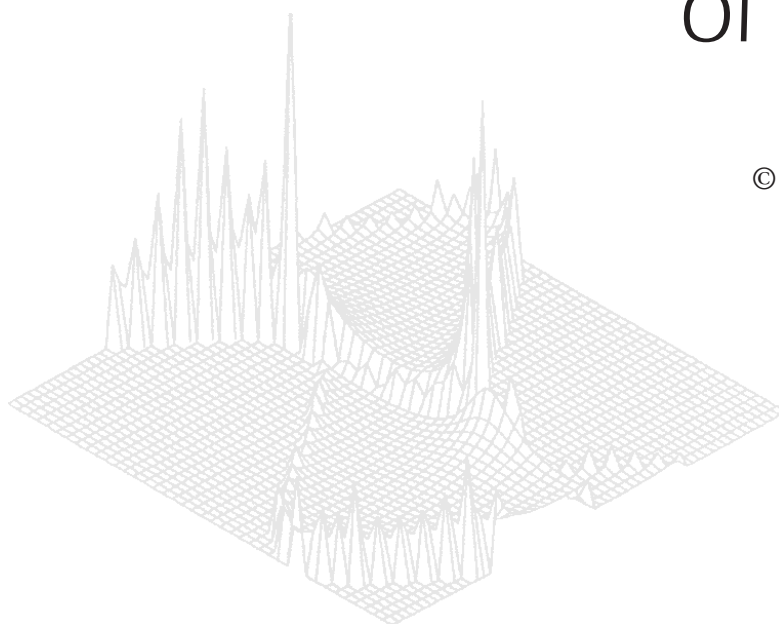
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## Valence of the Elemental Transition Metals\*

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### Abstract

We propose that the recently introduced bonding valence is the appropriate valence for describing the gross energetics of the elemental transition metals. In support of this proposal, we show that the trends in the experimental cohesive energies, surface energies and melting points of the noble and transition metals are simple linear functions of the bonding valence. The trends in the cohesive energies of the elemental transition metals are given by  $2.45Z_B - 3.47$  eV, where  $Z_B$  is the bonding valence.

### 1. Introduction

The unique properties of metals arise due to the delocalisation and condensation of the conduction electrons into the Fermi sea. The question arises: ‘How many electrons does a given atom contribute to the Fermi sea?’ That is: ‘What is an atom’s valence in a metal?’ For some elemental metals, such as Na or Al, the distinction between loosely bound ‘conduction’ and tightly bound ‘core’ electrons seems clear. For these ‘simple’ metals, the valence is conventionally set equal to the number of ‘conduction’ electrons. For other metals, the distinction is not so clear. For example, the noble metals apparently contribute both loosely bound s-electrons, as well as more tightly bound d-electrons. The situation is even murkier for the transition metals. How many electrons does Os or Ti contribute to the Fermi sea? Should one count all of the d-electrons for a given transition metal or only part of them?

We approach this question with the following remark. The conventional electron gas, jellium, cannot be applied in a consistent manner to inhomogeneous metals: for example, jellium fails to properly describe metal clusters, voids, surfaces, etc. The inconsistency arises because bulk jellium is kept uniform by non-physical external forces, and there is no clear prescription for uniquely choosing these forces if the metal is inhomogeneous. This problem was resolved in the early 1990s by the introduction of two new and nearly identical electron gas models (Shore and Rose 1999), the ideal metal model (Rose and Shore 1991; Shore and

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Rose 1991*a*, 1991*b*; Soler 1991) and the stabilised jellium model (Perdew *et al.* 1990) (for simplicity the ideal metal from hereon). The ideal metal naturally extends jellium to inhomogeneous metals, and is almost always more accurate even though it is no more difficult to calculate. The ideal metal should *always be preferred to jellium*.

*A priori* the ideal metal model is most suited to the simple metals. Useful results have been found for a whole range of simple-metal properties: chemical potentials, surface energies, work functions, surface plasmon excitations, vacancy and void formation energies as well as the ground state energy of small atomic clusters (see Shore and Rose 1999 for citations). The only inputs to the model are the valence of the metal and its specific volume per atom. Perhaps surprisingly, transition and noble metal cohesive energies (Rose and Shore 1991, 1994) and elastic constants (Rose and Shore 1993) can also be understood in terms of the ideal metal model provided an appropriate definition is provided for the valence for transition metals (Rose and Shore 1991, 1993, 1994).

Historically valence has been defined by the question ‘How many electrons per atom participate in the bond?’ In addition, one almost always makes the further simplifying supposition that each of the valence electrons contributes equally to the bond energy. We hypothesise that the valence of transition metal atoms in metals can be usefully defined by considering the equivalent ideal-metal electron gas for a given elemental metal (simple, noble or transition). We ask the simpler question: ‘How many electrons does each metal atom contribute to the ideal metal?’ The answer to this question has been christened the ‘bonding valence’ and tabulated in previous work. If the valence, defined in this way, is to be very useful, it must satisfy the supposition mentioned above; namely each valence electron should contribute an equal amount to the bond energy, and consequently the bonding energy of the metal should be linearly related to the bonding valence. This is the hypothesis we test empirically in this paper. We find that the measured cohesive energies, surface energies and melting points of the transition and noble metals all very nearly fall on a straight line when plotted versus the bonding valence.

The bonding valence was defined as follows in Rose and Shore (1991, 1993, 1994). Consider an infinite space of an elemental metal with its atoms on the ground state lattice sites. Measure the average electron density at the boundary of the real-space Wigner–Seitz cell that surrounds each atom. The average electron density  $n$  for the ideal metal model is defined to be the average density at the cell boundary in the actual metal. The bonding valence  $Z_B$  is defined to be the number of electrons that each atom contributes to the ideal metal, i.e.

$$Z_B \equiv n\Omega, \quad (1)$$

where  $\Omega$  is the volume per atom in the zero-temperature ground-state elemental metal. A measurement of the cell-boundary electron density in the actual metals would be needed to evaluate these definitions precisely. Since, up to the present time, electron densities cannot be measured with sufficient accuracy, Rose and Shore (1991, 1993, 1994) used the expedient of estimating these densities from first-principles muffin-tin density-functional calculations. The bonding valences of the metals are tabulated in Fig. 1 for the convenience of the reader.

Li (1.09) (3.15)	Be 1.99 1.88	ELEMENT BONDING VALENCE DENSITY PARAMETER											
Na (1.11) (3.80)	Mg 2.08 2.65											Al (2.76) (2.12)	
K (1.21) (4.57)	Ca 2.22 3.16	Sc 2.85 2.37	Ti 3.20 2.07	V 3.45 1.86	Cr 3.53 1.76	Mn 3.41 1.79	Fe 3.32 1.79	Co 3.09 1.80	Ni 2.83 1.84	Cu 2.57 1.95	Zn 2.40 2.17	Ga (2.43) (2.35)	Ge
Rb (1.24) (4.87)	Sr 2.32 3.39	Y 3.21 2.55	Zr 3.75 2.16	Nb 4.14 1.91	Mo 4.42 1.79	Tc 4.24 1.76	Ru 4.05 1.76	Rh 3.67 1.82	Pd 3.15 1.96	Ag 2.70 2.17	Cd 2.48 2.41	In (2.51) (2.57)	Sn
Cs (1.28) (5.18)	Ba 2.51 3.42	La 3.50 2.58	Hf 3.97 2.08	Ta 4.51 1.86	W 4.79 1.75	Re 4.79 1.70	Os 4.72 1.69	Ir 4.36 1.74	Pt 3.90 1.84	Au 3.26 2.03	Hg 2.53 2.46	Tl 2.38 2.68	Pb 2.35 2.75

**Fig. 1.** Input parameters for the theory of ideal metals, a uniform electron-gas model suitable for transition metals.

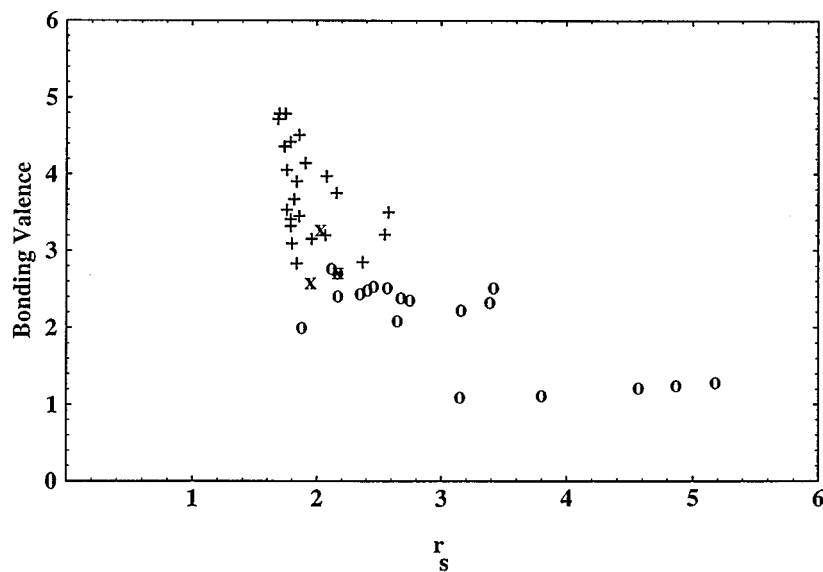
The contents of this paper are closely related to the empirical work of Miedema and others (Miedema and Boom 1978; Miedema *et al.* 1980; de Boer *et al.* 1988; Miedema 1992). These authors studied the energetics of metals and their alloys by imagining that each atom was just a small piece of the macroscopic metal. They christened the resulting method ‘the macroscopic atom’ model. This model, like our work, is parametrised in terms of the electron density of the cell boundary and the specific volume per atom. The work by Miedema *et al.* has enjoyed great success in predicting the properties of the elemental metals and especially the heats of formation of alloys. The major conceptual difference in our work results from the introduction of the ideal metal electron gas, and the natural definition of the bonding valence as the number of electrons that each atom contributes to that electron gas.

The electron density at the cell boundary was one of Miedema’s key variables. It is interesting to see if this variable is independent of the bonding valence—or whether the two parameters measure essentially the same thing. The density is described by  $r_s$  [ $r_s a_B \equiv (3/4\pi n)^{1/3}$ ], where  $a_B$  denotes the Bohr radius. Fig. 2 shows a plot of the bonding valence as a function of  $r_s$ . There is no evident correlation between  $Z_B$  and  $r_s$ ; consequently, we conclude that  $Z_B$  and  $r_s$  measure different aspects of the problem.

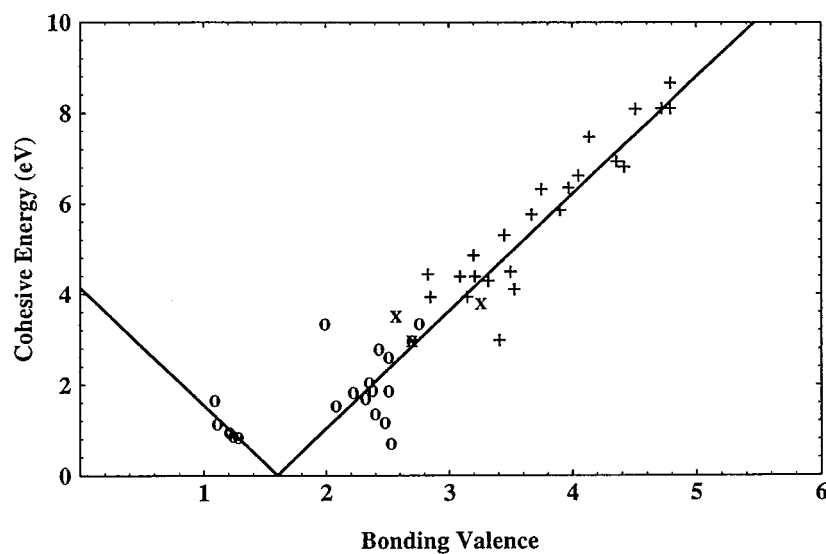
The structure of this paper is as follows. In Section 2 we plot the cohesive energies, surface energies and melting points as functions of  $Z_B$ . In Section 3 we discuss the empirical correlations discovered in Section 2 and relate them to the basic heuristics of the theory of ideal metals. Finally, we conclude the paper with a brief summary.

## 2. Correlating the Bonding Valence with Energies

The experimental cohesive energies  $\Delta E$  of the simple, noble and transition metals (Kittel 1971) are plotted against the bonding valence in Fig. 3. There is a clear linear correlation of the experimental cohesive energies with the bonding valence. For all of the metals, excluding the alkalis, the trend is for the cohesive energy to rise as the bonding valence increases. For the alkalis the cohesive energy decreases as the bonding valence increases. The cohesive energies were fit to



**Fig. 2.** Bonding valence as a function of  $r_s$ . The plusses represent transition elements, the crosses noble metals, and the circles simple metals.



**Fig. 3.** Cohesive energies of elemental metals as a function of the bonding valence. The plusses represent transition elements, the crosses noble metals, and the circles simple metals. The line represents the fit given by equation (2).

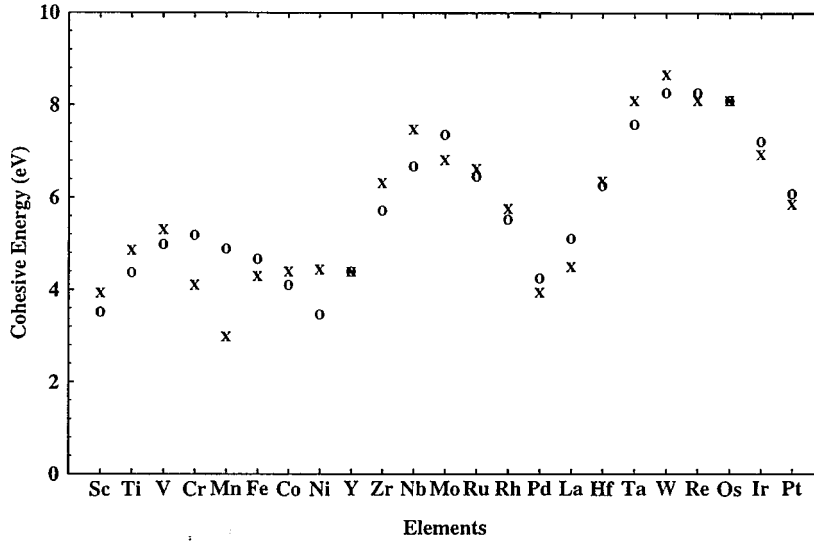
$$\Delta E \approx |2.6Z_B - 4.15| \text{ eV}, \quad (2)$$

shown by the line in Fig. 3. The fit to the cohesive energies of the transition, noble and alkali metals is good. However, the fit to the cohesive energies of the other simple metals is questionable.

In this paper, we will focus primarily on the transition and noble metals. The cohesive energies of these metals can be fit to

$$\Delta E \approx 2.45Z_B - 3.47 \text{ eV}. \quad (3)$$

Fig. 4 shows the quality of the fit given by equation (3) for the transition elements excepting  $T_c$ . The fit is quite good and exhibits the tendency of the energy to peak in the centre of the 3d, 4d and 5d series. The fit also shows that the cohesive energies increase as one moves from the 3d to the 4d to the 5d series. The largest discrepancies occur for the magnetic elements in the 3d series.



**Fig. 4.** Experimental cohesive energies of the transition metals compared with the fit given by equation (3). The crosses represent the experimental values, while the circles are the result of the fit. The major deviations occur for the magnetic 3d elements.

The experimental surface energies  $\sigma$  of many elemental metals have been estimated to approximately  $\pm 20\%$  by Tyson and Miller (1977). The surface energy is the energy per unit area. In order to obtain a quantity proportional to the energy, we considered the product of the surface energy and  $r_s^2$ . Fig. 5 plots  $\sigma r_s^2$  versus  $Z_B$  for 41 simple, noble and transition elements. A linear fit, shown by the line

$$\sigma \approx \frac{(2045Z_B + 500)}{r_s^2} \text{ erg cm}^{-2}, \quad (4)$$

suffices for all but two of the metals considered (Mn and Li). Fig. 6 shows the quality of the fit for 20 transition metals, the others were excluded for lack of experimental data. The fit is excellent except for Mn near the centre of the 3d series. Equation (4) fits most of the data fairly accurately. However, it appears to violate the trend for the alkali metals, whose surface energy decreases with increasing  $Z_B$ .

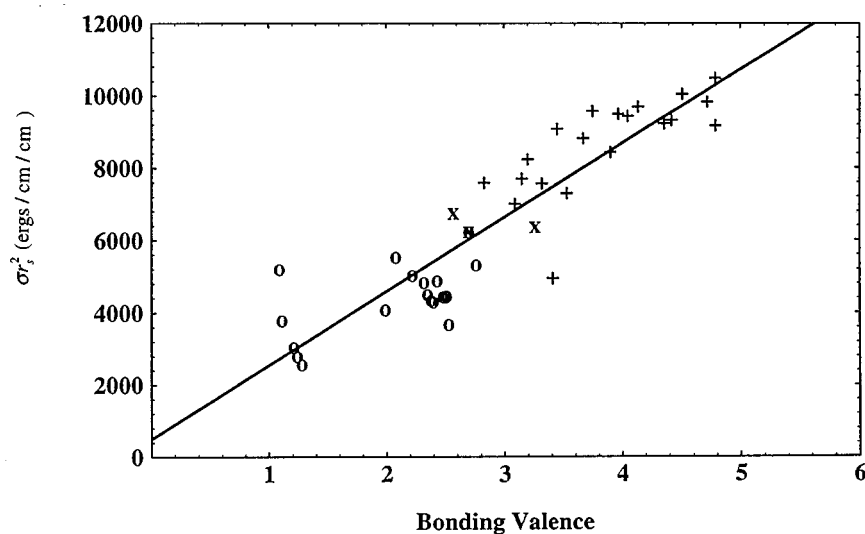


Fig. 5. Product of the surface energy and the square of the density parameter,  $\sigma r_s^2$ , for the elemental metals as a function of the bonding valence. The plusses represent transition elements, the crosses noble metals, and the circles simple metals. The straight line represents the fit given by equation (4).

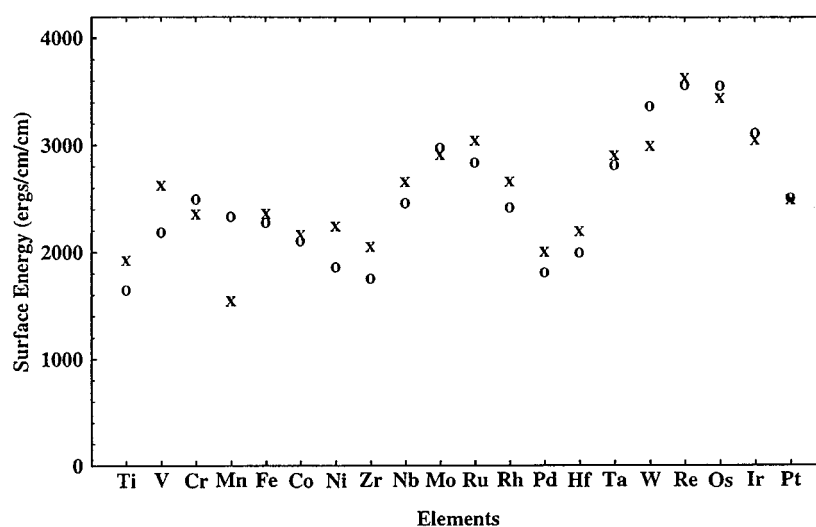


Fig. 6. Experimental surface energies of the transition metals with the fit given by equation (4). The crosses represent the experimental values, while the circles are the result of the fit. The major deviation occurs for Mn, a magnetic 3d element.

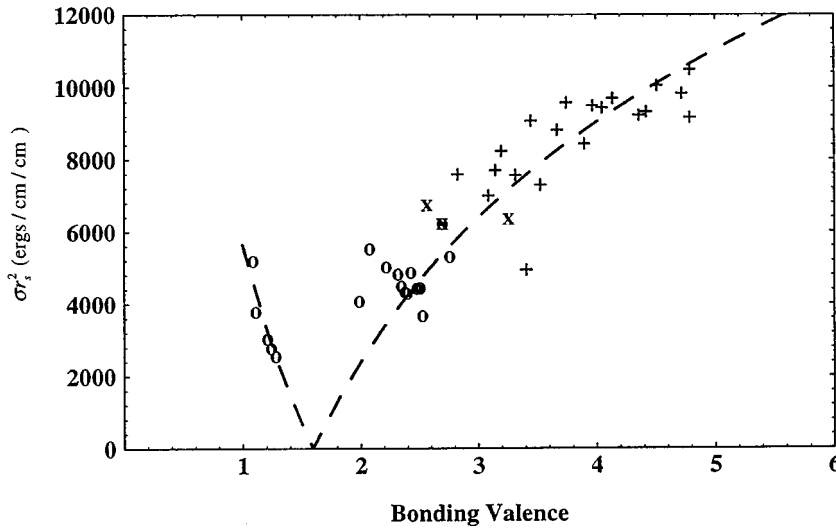
It is possible to find a fit that more accurately represents the trend for the alkali metals from the empirical relation (Tyson 1975; Rose *et al.* 1983)

$$\sigma \approx 0.80 \frac{\Delta E}{4\pi r_{WS}^2}. \quad (5)$$

Here  $r_{WS}$  denotes the Wigner–Seitz radius and is related to the density parameter by  $r_{WS} = Z_B^{1/3} r_s$ . Upon combining (2) and (5), we find

$$\sigma \approx 4.58 \times 10^4 \frac{|2.6Z_B - 4.15|}{4\pi r_s^2 Z_B^{2/3}} \text{ erg cm}^{-2}. \quad (6)$$

The quality of the fit using equation (6) is shown by the dashed line in Fig. 7. A good fit is obtained for the alkali, noble and transition metals. The fit to the other simple metals is somewhat less good than equation (4).



**Fig. 7.** Product of the surface energy and the square of the density parameter,  $\sigma_s^2$ , for the elemental metals as a function of the bonding valence. The plusses represent transition elements, the crosses noble metals, and the circles simple metals. The dashed curve represents the fit given by equation (6).

The melting points of the simple, noble and transition elements are plotted versus  $Z_B$  in Fig. 8. The noble and transition metals can be fit by

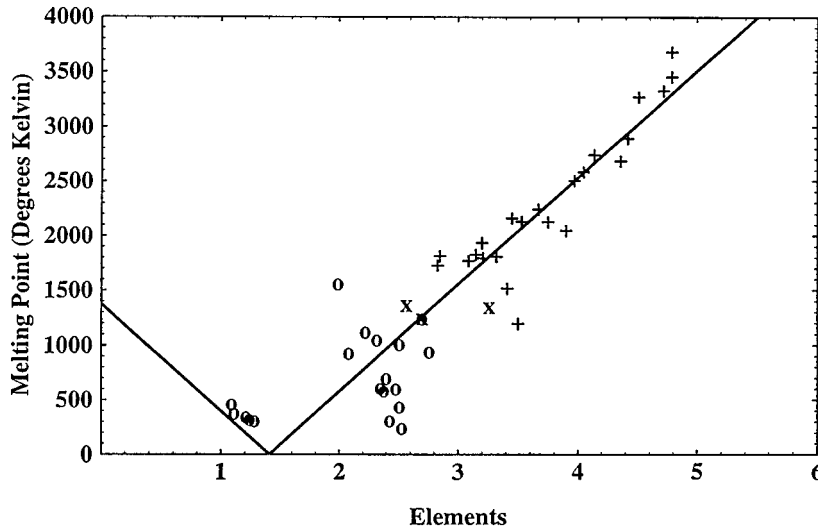
$$T_M \approx |977Z_B - 1376| \text{ K}, \quad (7)$$

shown by the straight line. A good correlation is evident for the noble and transition metals.

### 3. Empirical Relations and Heuristics of the Theory of Ideal Metals

We observed in the last section that the trends in the melting points, surface energies and cohesive energies of the noble and transition metals can be fit to linear functions of the bonding valence. In this section, we relate these empirical observations to the heuristics of the theory of ideal metal since this is the uniform electron gas model that defines the bonding valence and since the theory of ideal metals gives a reasonably good description of the cohesive energies of the transition metals.





**Fig. 8.** Melting points of the elemental metals as a function of the bonding valence. The plusses represent transition elements, the crosses noble metals, and the circles simple metals. The straight line represents the fit given by equation (7).

The ideal metal was derived from the uniform electron gas by requiring that no forces act on the positive background when the positive background is cleaved. That is, the electrons should not be under pressure in the uniform state. The ‘zero pressure’ condition was achieved by requiring that the electrons interact with the positive background not only electrostatically but also via a piece-wise constant local potential. This potential is chosen to be proportional to the background density of positive charge. The overall strength of the potential is set by the condition that zero force acts on the positive background in the uniform state. The uniform state of the ideal metal is defined entirely by one parameter, the electron density. The bonding valence enters if we split the ideal metal into pieces that are supposed to represent the atoms of particular metals.

The energy per electron of the uniform ideal metal  $e_i$ , as a function of the equilibrium density  $n_0$ , is the starting point of our analysis. Before we start, we must clarify that there are two ways  $e_i$  might be defined. First, one might (although we will not) imagine choosing an ideal metal suitable for some definite  $n_0$ . One might then ask: ‘What is the energy per electron for non-equilibrium densities  $n$  that differ from  $n_0$ ?’ The energy defined in this way is described in Shore and Rose (1999). In the present paper, we ask a quite different question. We suppose that we know the energy per electron not only for some particular equilibrium density, but also for all different equilibrium densities  $n_0$ . We ask: ‘What is the energy per electron as a function of the equilibrium electron density  $n_0$ ?’ We introduced  $n_0$  to indicate the equilibrium density and  $n$  to denote a non-equilibrium density only for the purposes of making the distinctions discussed in this paragraph. For the rest of the paper, we will denote the equilibrium density by  $n$ .

By definition  $e_i \equiv e_j + v_0$  for the uniform state, where  $e_j$  denotes the energy per electron in jellium and  $v_0$  denotes the energy due to the additional confining potential. Explicitly, from Shore and Rose (1999), we get

$$e_i(n) = e_j(n) - \frac{\partial e_j(n)}{\partial n}. \quad (8)$$

The energy per electron in jellium is usually expressed as the following sum of kinetic, exchange and correlation energies:

$$e_j(n) = an^{2/3} - bn^{1/3} + e_{c,j}(n). \quad (9)$$

The energy per electron in the ideal metal follows from (8) and (9):

$$e_j(n) = \frac{a}{3}n^{2/3} - \frac{2b}{3}n^{1/3} + e_{c,i}(n). \quad (10)$$

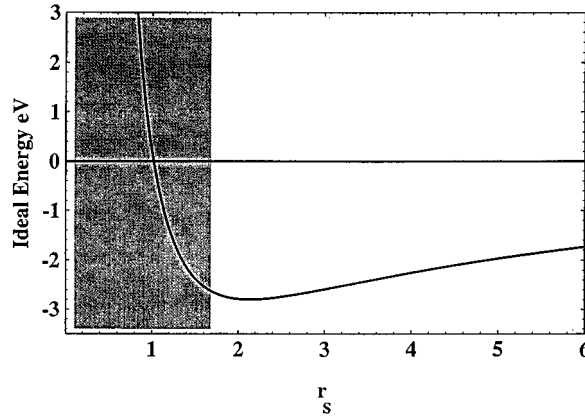
Here  $e_{c,i}(n)$  denotes the correlation contribution to the ideal energy. The following equation approximates the ideal energy:

$$e_i(r_s) \approx \frac{0.737}{r_s^2} - \frac{0.611}{r_s} + e_{c,i}(r_s) \text{ Ryd.} \quad (11)$$

Here

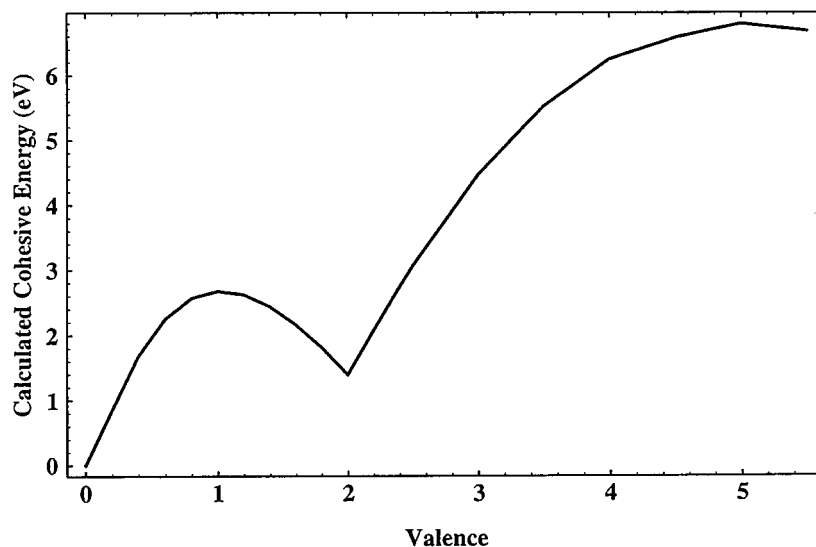
$$e_{c,i} = -0.045 \left\{ (2x^2 + 1) \log \left( 1 + \frac{1}{x} \right) - \frac{2}{3} + x - 2x^2 \right\} \quad (12)$$

is obtained from the Gunnarson and Lundqvist (1976) parametrisation of the correlation energy, and  $x = r_s/21$ . There are more refined estimates of the uniform electron-gas correlation energy available in the literature. However, these refinements are immaterial on the scale of our approximations and the work of Gunnarson and Lundqvist leads to a simple closed form formula for the ideal metal.



**Fig. 9.** Ideal energy as a function of  $r_s$ . No elemental simple, noble or transition metals have  $r_s$  values corresponding to the shaded region, where the energy curve is rapidly rising.

A plot of the ideal energy per electron calculated from equation (11) is shown in Fig. 9. The ideal energy has a minimum of  $-2.8$  eV near  $r_s = 2$ . The curve is slowly varying and negative over the range of  $r_s$  ( $1.68$  to  $5.18$ ) used to model the simple, noble and transition elemental metals. For large electron densities,  $r_s$  less than  $1.7$ , the ideal energy increases rapidly and becomes positive near  $r_s = 1$ . The energy per 'atom' in the uniform state of the ideal metal is  $Z_B e_i(n)$ . None of the elements have  $r_s$  values corresponding to the rapidly rising portion of the energy curve, since they could lower their energy by expanding and reducing the electron density in the bonding region.



**Fig. 10.** Cohesive energy of an elemental metal with  $r_s$  of 2 as a function of the bonding valence as calculated from the theory of ideal metals. The two maxima correspond to half-filled s- and p-shells.

The cohesive energies of the transition and noble metals increase by roughly  $2.5$  eV per additional valence electron. This increase in cohesive energy is roughly equal to the energy per electron of the ideal metal over the metallic range.

The simple metals cohesive energies correlated less well with a linear relation than did the noble and transition metals. In fact, the cohesive energies of the alkali metals decreased with increasing  $Z_B$  contrary to the observation for the noble and transition metals. This can be explained in part by examining the calculation of the cohesive energy using the theory of ideal metals. In that theory, one imagines that the uniform ideal metal consists of Wigner-Seitz cells of uniform positive background stacked together. The energy of the uniform metal is modeled as  $Z_B e_i$ . The energy of the atom is modeled by separating each Wigner-Seitz cell to infinity, replacing it with a spherical ball of positive background and computing the energy using the local density approximation to density functional theory.

The ideal-metal cohesive-energy is shown as a function of the bonding valence in Fig. 10 for  $r_s = 2$ . The maxima at  $Z_B = 1$  and 5 correspond to a half-filled s-shell and a half-filled p-shell for the spherical ball of positive charge used to

represent the atom. The minimum at  $Z_B = 2$  corresponds to the increased stability corresponding to the filled s-band. Consequently, we see that within the theory of ideal metals, the cohesive energies of the alkali metals decrease with increasing bonding valence, as observed experimentally. Similarly the ideal metal agrees with experiment and predicts that the cohesive energy increases for the noble and transition metals as the number of bonding electrons increases from two to five.

#### 4. Summary

The cohesive energies, the surface energies and the melting points of the noble and transition metals have been shown empirically to be simple linear relations of the bonding valence. The existence of these empirical correlations confirms the fundamental physical significance of the bonding valence. They suggest that the definition of the valence given by equation (1) is the one that is appropriate for elemental transition metals. It will be of interest to see if the bonding valence usefully describes transition metal alloys as well. In the first paragraph of the Introduction, we asked rhetorically: ‘How many electrons does Os or Ti contribute to the Fermi sea?’ We can now answer that Os contributes 4.72 electrons, while Ti contributes 3.20.

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