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Brief Reports

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Uniform electron gas for transition metals: Input parameters

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Input parameters are reported for the theory of ideal metals, a uniform electron-gas model of the elemental transition metals. These input parameters, the electron density, and the "bonding valence," have been given previously for the 3*d* and 4*d* series of transition metals. Here, we extend our work based on recent calculations of Sigalas *et al.* [Phys. Rev. B **45**, 5777 (1992)] to include the 5*d* series. We have also calculated the cohesive energies of the 5*d* transition metals using the theory of ideal metals with these parameters. The calculations agree with experiment to within ±25%.

The cohesive energies of the 3*d* and 4*d* transition metals were recently calculated using the theory of ideal metals, an electron-gas model.[1] The results were surprisingly good given the simplicity of the theory, which modeled the metal as a uniform electron gas and the atom as a ball of positive charge with a compensating number of valence electrons. The input parameters to the theory of the ideal metal are the electron density and the number of electrons per atom (the "bonding valence"). These input parameters were provided in Ref. 1 for the metallic elements through the 4*d* series. In this paper, we extend the list of input parameters for the metallic elements through Pb in the 5*d* series.

The electron-gas model has recently been extended by requiring that no forces act on the positive background in the uniform state. Two slightly different extensions of the electron gas have emerged. These models have been named "pressure stabilized jellium" by Perdew, Tran, and Smith[2] and the "theory of ideal metals"[1,3,4] by us. The feature introduced by the theory of ideal metals is an additional interaction between the electrons and the positive background. This additional interaction is provided by an electron potential, $v_0(\mathbf{r})$, that is strictly proportional to the background charge at $\mathbf{r}$. The strength of this additional potential is determined by the condition of mechanical equilibrium, i.e., by requiring that there are no forces on the positive background in the uniform state. Although no new parameter is needed to fix the additional potential, v_0 has the effect of including parts of the electron-ion interaction that are neglected in jellium. Details are found in Refs. 1–4.

The theory of ideal metals allows one to understand the trends in the cohesive energies of the elemental metals without explicit reference to the ion core. That is, there is no explicit input of core properties such as the core charge, the *s*, *p*, or *d* nature of the valence electrons, or the parameters that define a pseudopotential. The ground state of the metal is treated as a uniform electron gas, which is basically defined by its density.

The theory of ideal metals is parametrized by the uniform electron density and the bonding valence. We report the density parameter, r_s ($4\pi r_s^3/3 = 1/n$, where n is the density), as well as the bonding valence Z_B, which is defined as the atomic volume times the average electron density. Z_B indicates the number of electrons that each atom contributes to the electron gas.

In this paper, we first suggest bonding valences and density parameters for the elemental metals. Next, we report calculations using the theory of ideal metals for the cohesive energies of the metallic elements (Cs-Pb) in the 5*d* series. Finally, we briefly discuss the reliability of the input parameters assigned to various elements and conclude with a summary.

We have previously reported "suggested" bonding valences and density parameters for the 3*d* and 4*d* series of elemental metals, based on first-principles density-functional calculations of Moruzzi, Janak, and Williams[5] for the ground state of these elements. Moruzzi, Janak, and Williams[5] noted that the density at the cell boundary could be used to semiempirically predict the bulk modulus. More recently, the ground-state energies and densities of the 3*d* (Ca-Zn), 4*d* (Sr-Cd), and 5*d* (Ba-Pb) series of metals were computed by Sigalas, Papaconstantopoulos, and Bacalis[6] using a scalar-relativistic augmented-plane-wave method and a muffin-tin approximation. They computed the ground state of each element

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TABLE I. Input parameters for the theory of ideal metals, a uniform electron-gas model suitable for transition metals.

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

for both bcc and fcc lattices. They provided us with the number of interstitial electrons[7] (i.e., the number of electrons outside the muffin tin, but inside the unit cell), an unpublished output of their code.

The density parameter and bonding valence were inferred as follows. First, we defined the average electron density n by dividing the number of the interstitial electrons by the volume of the interstitial region. The interstitial volume was computed from the measured lattice parameter reported in Kittel.[8] Second, we defined the bonding valence as the product of the electron density, n, and the volume per atom, V, in the metal. The bonding valence is

$$Z_B = nV \ . \tag{1}$$

The bonding valence and density were inferred from the appropriate calculation of Sigalas, Papaconstantopoulos, and Bacalis[6] for metals with fcc or bcc symmetry. For the other elements, we report the result inferred from the fcc calculation, since most of the remaining metals have hcp symmetry and are nearly close packed.

Table I gives the density parameters and bonding valences. The elements, whose parameters are in parentheses, were not computed by Sigalas, Papaconstantopoulos, and Bacalis. These input parameters have been taken from Ref. 1 with the exception of Cs. For Cs, we estimated the parameters by extrapolating from K and Rb. For the most part, the bonding valence increases as one proceeds down the columns of the Periodic Table. We attribute this to the expulsion of the valence electrons (due to the Fermi exclusion) from the increasingly larger cores. Integer valences have traditionally been assigned to the simple metals, and these can be compared with the values presented here. The bonding valences for the nominally divalent simple metals are increased from 2, and Z_B ranges from 1.99 for Be to 2.51 for Ba. The bonding valences are also larger than 1 for the monovalent alkali metals; Z_B ranges from 1.09 for Li to 1.24 for Rb. The bonding valence of nominally trivalent thallium was reduced to 2.38, while nominally tetravalent lead has a bonding valence of only 2.35. The deviation of the valence of lead from its nominal valence was the largest for any of the simple metals.

The parameters in Table I are based on an attempt to infer the average density of electrons at the boundary of the unit cell. In principle, this average density could be measured, and such a measured value would be preferred. In any case, the parameters reported in Table I must be considered somewhat provisional, especially for those elements whose ground states do not have bcc and fcc symmetry. Presumably, the input parameters are fairly accurate for those elements that have an hcp ground state with a nearly ideal ratio of c axis to a axis. The input parameters for other hcp's (such as Cd, Mg, and Zn, whose

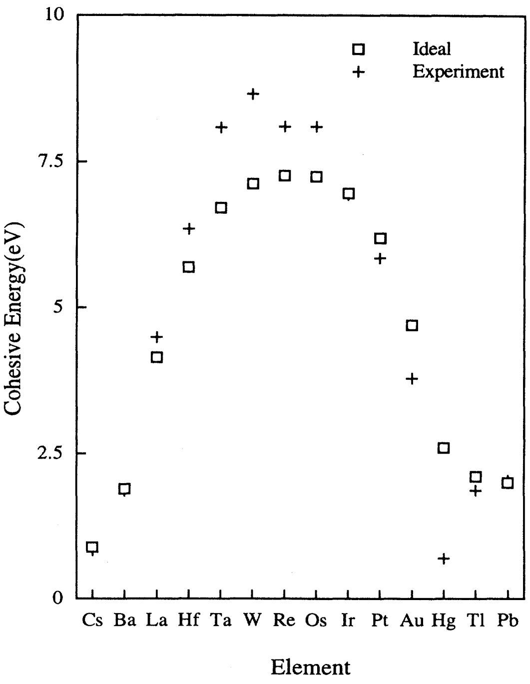

FIG. 1. Cohesive energies calculated using the theory of ideal metals and the input parameters in Table I, and a comparison with experiment.

c/a ratio is far from ideal) are questionable. The assignments for Mn (cubic complex), La (hexagonal), Hg (rhombehedral), Ga (complex), and In (tetragonal) are also provisional. Similar reservation must be noted concerning the ferromagnetic elemental metals (Fe, Co, and Ni) since their parameters were estimated from a paramagnetic calculation.

The cohesive energies of the $5d$ transition metals were calculated using the parameters in Table I. The ground state of the metal was modeled by the uniform ideal metal. The atom was modeled by a small spherical ball of uniform positive background charge (its radius determined by the atomic volume in the metal) and a compensating number of electrons. The charge of the positive background and the number of electrons was determined by the bonding valence. The energy of the model atom was determined by using the Kohn-Sham[9] theory and the local-density approximation. Details are given in Ref. 1.

The calculated cohesive energies are shown in Fig. 1 and agree with experiment to within 25% for the transition metals. This seems to us a remarkable result, especially when taken together with the similar, previously reported results for the $3d$ and $4d$ series. It implies that the cohesive energies of the elemental transition metals depend primarily on the electron density in the bonding region and the atomic volume. These simple parameters substantially account for the effects of the core electrons on the cohesive energy.

Errors larger than 25% in the calculated cohesive energies occurred for Hg in the present calculation and for Zn, Cd, Be, Mn, and Cr in Ref. 1. These errors are not too surprising given the errors in estimating the input parameters of Cd and Zn, which have an hcp crystal structure which is far from ideal, and for Mn and Hg whose crystal structures are neither bcc, fcc, nor hcp. The errors for Be and Cr must presumably be attributed to the overly simple nature of the theory of ideal metals.

Input parameters have been given for a uniform electron-gas model of the transition metals. We feel that the present model (or a more sophisticated variant) should replace the conventional electron-gas model (jellium) for all calculations that model inhomogeneous metals.

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