current flowing in B results in a further depression of f and the continuity conditions imposed at the boundaries require that f in A should also be depressed further, thereby leading to a decrease in the critical current I_{cA}.

The difference in the reduction of I_{cA} due to I_B flowing in two relative directions arises from the different pair density distributions in the region which connects the two SWL's. When currents in the two SWL's are opposite and meet in the middle of the system, their influence on the depression of $f(y)$ in the middle is less effective than in the case when the two currents are in the same direction. Hence, the curve for currents flowing against each other should lie above that for currents flowing in the same direction. The curves shown in Fig. 3 are in good qualitative agreement with experimental results.[1,11] The stationary interaction thus explains the symmetric part[1,2] of critical-current depression in the $V=0$ region.

In conclusion, we have shown explicitly that the stationary interaction between two SWL's gives rise to coherent behavior of the system when the separation is around one coherence length. The decrease in critical current of one SWL due to pair-density depression originating from a current in a neighboring SWL is in good agreement with experiment. Details of the present calculation will be presented in a separate publication.

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Orbital Model of Thermochemical Parameters

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A thermochemical scheme containing two adjustable variables per element has been developed by Miedema and co-workers which correctly predicts the signs of the heats of formation of 500 binary metallic alloys. Here we propose a simple but l-dependent orbital quantum model based on the valence energies of hydrogenic ions which contains *no adjustable elemental variables* and which fits the Miedema variables for 25 simple metals with an rms accuracy of 3%.

Some of the central questions in condensed-matter physics are thermochemical in nature and involve the existence and the crystal structures of binary compounds and alloys. Although quantum mechanics provides us with a general recipe for answering these questions (at least in principle) for any individual system, a central theoretical goal has been the development of atomistic concepts which will predict global trends in all possible binary interactions in terms of separable elemental parameters. If we consider the global ensemble of all such binary combinations, the number of possibilities is so great and the distinctions in energy so fine as to preclude the development of a deductive, quantum-mechanical solution from "first principles." Thus the literature abounds with atomistic empirical schemes of one kind or another, and often there seem to be no criteria which can distinguish among them. While it may be difficult or impossible to use quantum mechanics to *derive* valid thermochemical atomistic concepts, we may be able to employ quantum-mechanical methods to *test* the accuracy of global schemes with great precision. In this Letter we report the results of such a test which go far beyond what has been achieved in this area by the entirely deductive approach. We establish direct relations between the electronic spectra of isolated atoms and thermochemical properties of atoms immersed in intermetallic alloys.

A cellular (Wigner-Seitz) thermochemical scheme for the heats of formation ΔH_f of liquid and solid metal alloys has been developed by Miedema and co-workers.[1] The scheme successfully predicts the signs of ΔH_f for 500 binary alloys constructed from 53 metallic elements. The two basic elemental variables are φ^*, which measures the chemical potential (or work function or electronegativity) of each elemental atom, and an entirely new thermochemical variable n which is thought to measure the electron density at the surface of the spherical atomic cell. The scheme treats only the isotropic or structurally averaged part of ΔH_f for the alloy ensemble. In this Letter we provide a simple quantum model for the 106 adjustable elemental variables of the Miedema scheme. Our model is based on spectroscopic valence energies of hydrogenic ions and contains *no adjustable elemental variables*.

The crucial feature of the Miedema scheme is that it contains contributions to ΔH_f of both signs. When the molar volumes are equal, $\Delta H_f(AB)$ is given by

$$\Delta H_f = -P(\Delta\varphi^*)^2 + Q(\Delta n^{1/3})^2 - R\theta_d\theta_s. \qquad (1)$$

Here $\Delta\varphi^*$ measures the difference in chemical potentials of A and B in the bulk. The metals are either simple metals (s) or transition metals (d), and $\theta_d\theta_s$ is 1 or 0 according to whether AB is or is not an s-d pair. The value of Q/P which determines the sign of ΔH_f for s-s and d-d alloys is $(3.07\ \text{eV})^2/(\text{density units})^{2/3} = 9.4\ \text{eV}^2/(\text{density units})^{2/3}$. In practice, φ^* and $n^{1/3}$ are treated as adjustable variables. To determine these variables and to justify the form of (1), Miedema and co-workers analyzed, corrected, and in some critical cases measured or remeasured phase diagram data from the massive alloy literature. We believe that this Herculean effort has been extraordinarily successful and that the empirical values of φ^* and $n^{1/3}$ in the Miedema scheme are by far the most accurate so far obtained in any global electrochemical or thermochemical scheme capable of computing the isotropic (nonstructural) contributions to intermetallic heats of formation.

There are several important conceptual questions about the Miedema scheme which concern the significance of his classical variables φ^* and n. For example, (i) the scientific literature contains many empirical tables of elemental electronegativities (one of the earliest tables, and still the most widely used, is due to Pauling[2]). The connection between electronegativity and work function φ is well known.[3] However, experimental work functions, which span a range $R(\varphi)$ of about 5 eV, are uncertain in general by as much as 0.5 eV for all but a few elements.[4] For metals, the Pauling electronegativity X spans a range $R(X) \sim 2$ and appears to be accurate (e.g., in differentiating crystal structures[5]) to about 0.1. Thus the Pauling scale is accurate to about 5% compared to experimental work-function accuracies of order 10%; this factor-of-2 improvement in accuracy is very important and may help to explain the very wide applications which are made of the Pauling table.

The overall range $R(\varphi^*)$ of Miedema's thermochemical variable φ^* is the same as $R(\varphi)$, but values are quoted to 0.05 eV, a 1% accuracy which (if it is correct) represents an improvement over experimental accuracies for φ of a factor of 10 and an improvement over the accuracy of Pauling's values of a factor of 5. The question is whether such gigantic improvements are meaningful; and because of the very wide applications which have been made of the Pauling scale, this is a most important question in the structure of solids. The problem, however, is to find an independent method for testing the Miedema variables to an accuracy of order 1% when all previous scales are accurate at best to 5%.

(ii) The new variable introduced by Miedema, $n(r_{\text{WS}})$, the electron density at the surface $r = r_{\text{WS}}$ of the Wigner-Seitz cell, replaces the atomic size r_{WS} as a critical metallurgical variable, and is not monotonically correlated[1] with r_{WS}. Thus altogether there are more than 100 adjustable elemental variables in the Miedema scheme for more than 50 metals. Moreover, there is considerable cancellation between $\Delta\varphi^*$ and $3\Delta n^{1/3}$ in the attractive P and the repulsive Q terms of Eq. (1). Are φ^* and $n^{1/3}$ truly independent elemental variables, and what is the microscopic origin of these thermochemical quantities?

To answer these questions we have developed a quantum model for φ^* and $n^{1/3}$ which expresses these elemental variables in terms of spectroscopic characteristics of the corresponding atomic cores. While our model contains parameters which couple spectroscopic quantum energies to classical thermochemical variables, these coupling parameters *are constant* for 25 simple metals. Because the spectroscopic energies are derived from the properties of isolated atoms, they provide an entirely independent basis for calibrating the significance of Miedema's 100+ elemental variables extracted from massive and almost exhaustive metallic alloy data; no such independent basis for calibrating thermochemical variables so precisely is known to us in previous work.

Our model is a refinement of the Simons–Bloch–St. John orbital (l-dependent, where l is the orbital angular momentum) shell model.[6] In this model the atomic cores are described by l-dependent core radii r_l, which are defined as follows. Consider the energy levels E_{Nl} of the hydrogenic ion with one valence electron outside a closed-shell (inert gas) core. These are represented by a Rydberg series with a quantum defect[7] $\delta_{N'l}$ which varies slowly with $N'=N+p$ (we are interested primarily in the case $p=0$),

$$E_{Nl} = -Z^2/2(N+\delta_{Nl})^2, \tag{2}$$

where the energies are in a. u. To derive r_l it is assumed that the principal quantum number N in the crystal is a good quantum number (i.e., that metallic or covalent hybridization of valence electrons mixes states with different l but with the *same* N). With this simple and conventional chemical assumption the pseudopotential for the hydrogenic ion of charge $+Z$ becomes, in a. u.,

$$V(r) = -Z/r + \hat{l}(\hat{l}+1)/2r^2, \tag{3}$$

and the energy levels are given by (2), provided that

$$\hat{l} = l + \delta_{Nl}. \tag{4}$$

The classical turning points of electrons at the Fermi energy ($=-\varphi$ in the metal and $=0$ for the free atom) are used[8] to define r_l from (3). They are

$$r_l = \hat{l}(\hat{l}+1)/Z, \tag{5}$$

where $\hat{l}$ is determined from E_{Nl} by (2) and (4). It is given in a. u.

The equations that we have used to connect the thermochemical variables φ^* and $n^{1/3}$ (in Miedema's units) to the orbital shell radii (in a. u.) are

$$\tilde{\varphi} - \tilde{\varphi}_0 = \sum_{l=0}^{2} \frac{a_l}{r_l}, \tag{6}$$

$$\tilde{n}^{1/3} - \tilde{n}_0^{1/3} = \sum_{l=0}^{2} \frac{b_l}{r_l}. \tag{7}$$

These equations are l-dependent generalizations of earlier models[3] for φ. The coupling parameters a_l and b_l are determined by least-squares fitting of the elemental thermochemical variables φ^* and $n^{1/3}$ by their spectroscopic analogs $\tilde{\varphi}$ and $\tilde{n}^{1/3}$. With the coupling parameters quoted below, these fits are accurate to 3% (rms) for φ^*.

By replacing 50 variables for 25 simple metals by 8 coupling parameters in (6) and (7), we have obtained a substantial simplification. We may also recognize that the thermochemical variables φ^* and $n^{1/3}$, or $\tilde{\varphi}$ and $\tilde{n}^{1/3}$, are nearly linear in Z only for elements belonging to the first (Li) period. The interplay between atomic subshells with different l in the later periods becomes increasingly complex, especially for the s electrons as they penetrate increasingly heavier atomic cores. (A well-known example in molecules is Pb, which may be either tetravalent or divalent, depending on whether or not the $6s^2$ subshell forms covalent bonds.) By using the orbital radii r_l in (6) and (7) we are able to separate the contributions of different valence subshells to Miedema's thermochemical variables. Because of the great reduction in the number of adjustable constants, we obtain an independent test of the validity not only of the values of his variables, but also of his novel and original formula (1) for heats of formation of intermetallic alloys.

To illustrate these points we examined Miedema's earlier values for φ^* obtained in 1973 from scattered and fragmentary values of φ. These are illustrated in Fig. 1 for the Cu, Ag, and Au periods. At this stage his values of φ^* decrease with increasing Z in these heavier periods. Fitting (6) to his 1973 simple metal values, we obtain

$$a_0 = 0.41, \quad a_1 = 0.15, \quad a_2 = -0.96, \tag{8}$$

a result that is *unphysical* because of the sign and magnitude of a_2. (After all, the d-electron contribution in any metal should have the same sign as the s and p contributions, and in simple metals its magnitude should be much smaller.) Miedema's final table (1975) contains 25 simple metals and includes significant revisions of his earlier values of φ^* to improve the agreement of (1) with experiment. These values are shown in Fig. 2, and now there is a minimum in $\varphi^*(Z)$ near $Z=2$ or 3 for these periods. By using Eq. (6) we are able to analyze the difference in the Z dependence of the thermochemical parameters in Figs. 1 and 2 in terms of a difference in l-dependent coupling constants. The rms fit to φ^*

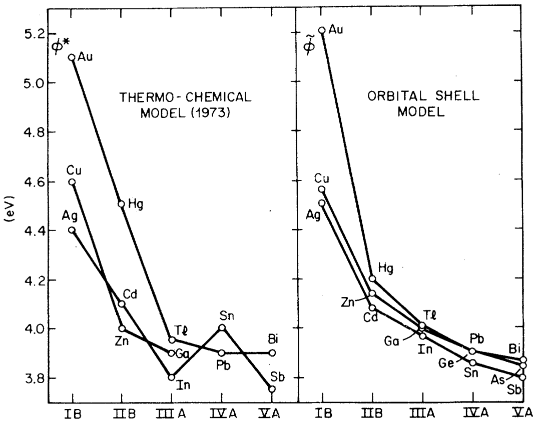

FIG. 1. The atomistic work-function variable φ^*, as derived in a preliminary empirical table (Ref. 1), has been fitted by the orbital shell model $\tilde{\varphi}$ as given by Eqs. (7) and (8).

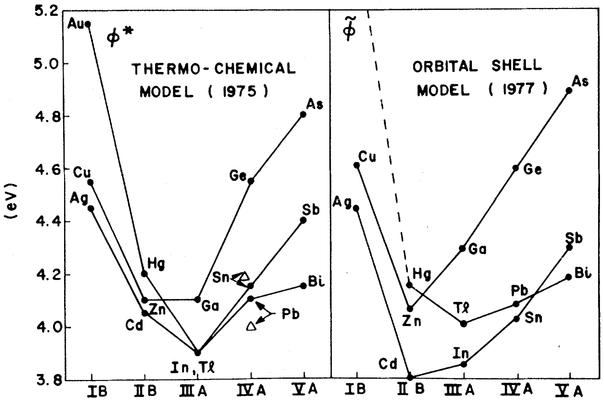

FIG. 2. The revised and refined values of φ^* have again been fitted by $\tilde{\varphi}$ using Eqs. (7) and (9). The difference between Figs. 1 and 2 arises because of different coupling constants (weighting factors) for different values of the orbital angular momentum.

(1975) for all 25 simple metals gave the results partially illustrated in Fig. 2 and determined the coupling constants as

$$a_0 = 1.24, \quad a_1 = 1.76, \quad a_2 = 0.22, \tag{9}$$

which is much more satisfactory. Not only is a_2 small and positive but the ratio of a_0 to a_1 is also close to what one would expect for simple metals ($Z = 1$ to 5, i.e., an average over s^2p^3 valence configurations). Thus the coupling parameters distinguish successfully between unphysical and physical thermochemical schemes. Moreover, a detailed analysis[8] of "worst cases" has led us to believe that Miedema's accuracy is indeed of order 1%. (The worst cases may be Pb and Sn, where errors of order 3% and 1% have been estimated, as illustrated in Fig. 2.)

A detailed analysis[8] of Miedema's second variable, $n^{1/3}$, shows that the representation (7) is accurate to only 6% and that 3% accuracy is obtained only when the right-hand side of (6) is multiplied by a factor containing the atomic radius r_{WS}. However, (7) is accurate enough to describe the large cancellation of the attractive and repulsive terms in (1). We find

$$b_l = 0.318 a_l - 0.041 \delta_{l1}, \tag{10}$$

where δ is the Kronecker delta. Substituting (6), (7), (9), and (10) in (1), we find ($\theta_s \theta_d = 0$)

$$\Delta H_f / P = -0.25 \Delta \tilde{\varphi} \{ 0.20 \Delta \tilde{\varphi} + \Delta [r_p^{-1}] \}. \tag{11}$$

Comparison of (11) with (1) shows that on the average more than 90% of the attractive term is canceled by the repulsive term.

In the large and active field of quantum-mechanical studies of crystal structure by "first principles," various approximations are often employed (phase shifts, muffin tins, local pseudopotentials, etc.). The very large cancellation exhibited by (11) indicates that these simplifications are unlikely to yield results for bulk or surface properties of thermochemical significance. On the other hand, calculations employing nonlocal pseudopotentials[8] derived from the orbital shell model would be of great interest.

We are grateful to A. N. Bloch and A. R. Miedema for helpful conversations.

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ERRATA

BEAM-DENSITY EFFECT ON THE STOPPING OF FAST CHARGED PARTICLES IN MATTER. R. A. McCorkle and G. J. Iafrate [Phys. Rev. Lett. 39, 1263 (1977)].

On page 1263, Eq. (1) should read $S_0 = -(Ze/a)^2 K_0(\rho/a)$.

On page 1265 the seventh line below Eq. (11), the term "neutrilization" should read "neutralization."

On page 1265, the third line above Eq. (12) should read $N_{ci} \simeq 2\pi n_i' a'^3/3$.

In Ref. 34, the inequality should read "$\omega_i/\omega_b \ll 1$."

STABILITY OF SUPERFLOW IN ^{3}He-A. P. Bhattacharyya, T.-L. Ho, and N. D. Mermin [Phys. Rev. Lett. 39, 1290 (1977)].

In the second sentence of the first paragraph following Eq. (7), the symbols K_b and c_0 should be interchanged. The point being made is unaltered by this transposition.

In Ref. 5, "boojum" should read "boojums."

OPTICAL ROTARY SATURATION. Yehiam Prior and E. L. Hahn [Phys. Rev. Lett. 39, 1329 (1977)].

On page 1331, line 4 of the first column "$\Delta\omega_l \gg \omega\mathcal{E}_l$" should read "$\Delta\omega_l \gg \kappa\mathcal{E}_1$" and near the bottom of the second column on the same page the phrase "field of a different frequency $\omega_2 \cos(\omega_l + \epsilon)t$" should read "field $\mathcal{E}_2 \cos(\omega_l + \epsilon)t$ at a frequency different from the strong field $\mathcal{E}_l = \mathcal{E}_1$ . . . ."