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Binding Energies of Transition-Metal Atoms Adsorbed on a Transition Metal

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The binding energies of transition-metal atoms of the 5*d* series adsorbed on a 5*d* transition metal are calculated in the tight-binding approximation. The general features of the variation of the binding energy with the number of adatom 5*d* electrons are similar for all the substrates. It shows a parabolic behavior with a maximum of the order of the cohesive energy for the substrate, and a subsequent sharper decrease as the number of adatom 5*d* electrons is increased. The maximum is always located close to tungsten, as in the case of a tungsten substrate, where it is between tungsten and rhenium.

Some measurements have been made recently of the binding energy[1] and diffusion[2] of third-transition-series metals on various single crystal planes of tungsten, using a field ion microscope technique. The binding energies were deduced from field-desorption data and are subject to some uncertainty in their quantitative determination.[3] However the rise in the adatom binding energy to a maximum for rhenium, similar to the maximum in the cohesive energies for 5*d* transition metals, and the subsequent sharper decrease as the number of adatom 5*d* electrons is increased seem now well established (Fig. 1).

Several attempts at attaining a theoretical understanding of the binding energy have already been made, based either on a tight-binding model,[4,5] or on a virtual-bound-state model.[6] Recently, Newns has also discussed the importance of correlation in this problem.[7]

It seems more reasonable to study the binding energy of transition-metal atoms on a transition metal, by using a tight-binding approach, as the tight-binding *d*-band-broadening contribution to the cohesive energy of transition metals dominates for the majority of transition metals.[8,9]

Here, we will calculate the binding energies of the 5*d* transition-series atoms on a 5*d* transition metal, using a tight-binding model, taking into account somewhat more realistically some parameters, such as the real crystalline structure of the substrate and the degeneracy of the *d* band. But consequently, we are only able to take into account self-consistency in a phenomenological way, and our results are particularly valid for adatoms having approximately the same number of *d* electrons as the substrate.

We use a moments technique, already used with some fair success to describe various properties of transition metals.[4,8,10] The method and the approximations have already been described elsewhere.[4,10] Let us just recall that we are using a Hartree scheme with a tight-binding description of the *d* band, neglecting the contribution of the *s* band and of *s*-*d* mixing. As usual, we use a two-center approximation involving two kinds of overlap integrals, the crystalline ones α, and the transfer type β, involved, respectively, in the shift of the *d* band and its width. The overlap integrals α and β are strictly defined as 5×5 matrices[10] but, in fact, due to the smallness of the crystalline ones, one can take an average value α equal to the shift of the band for them. On the other hand, following the notations of Slater and Koster,[11] and from the second moment, one can define the square of an effective overlap integral β^2 as $5\beta^2 = dd\sigma^2 + 2dd\pi^2 + 2dd\delta^2$. β^2 is also directly related to the width of the *d* band.[10]

One starts from a perfect transition-metal M surface and a free transition atom A, and then the atom A is absorbed on the surface of M, the coupling between them being established through the overlap integrals. The binding energy $U_B(A-M)$ of the adatom A can then be defined as the difference between the total energy before and after the atom A had been absorbed on M. Clearly the expression of $U_B(A-M)$ will involve the variation of geometry of the sys-

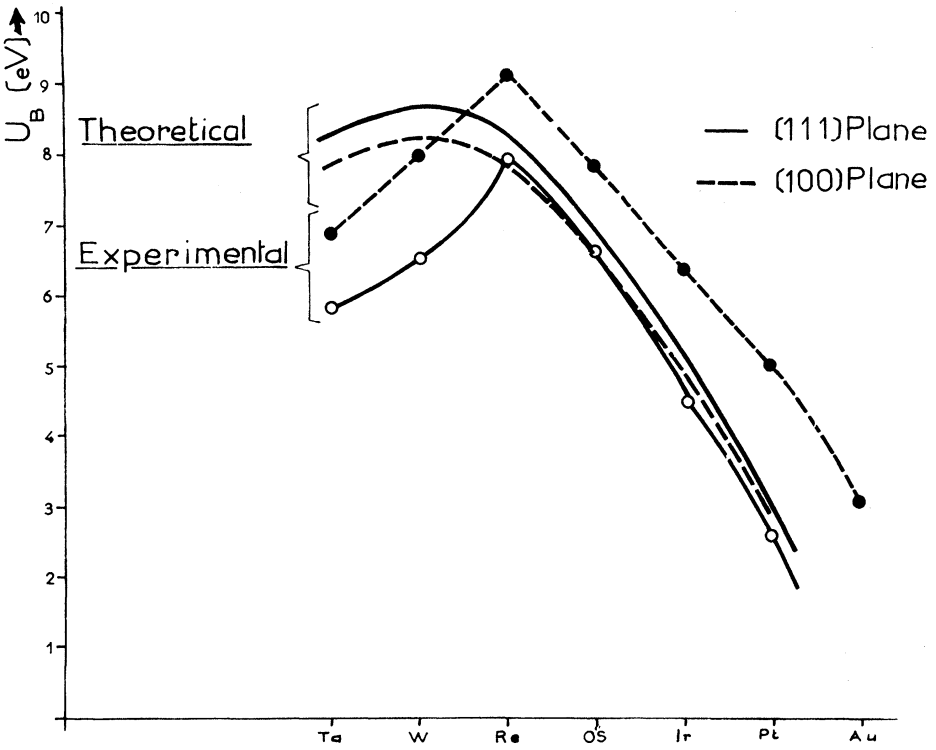

FIG. 1. Theoretical and experimental results (Ref. 1) for the binding energy of the 5*d* elements on the (100) and (111) planes of bcc tungsten.

tem when A is absorbed, the corresponding change in the overlap integrals, and the difference between the number of d electrons of A and M and of their energies.

For simplicity, we will divide the computation of $U_B(A-M)$ in two steps: the first one, the computation of the binding energy of an adatom M on the same metal surface M, $U_B(M-M)$, and the last one, its change due to the replacement of the adatom M by an adatom A:

$$U_B(A-M) = U_B(M-M) + \delta U(M \to A) \ . \tag{1}$$

Let us first give some definitions useful in the following: The semi-infinite metal M has N atoms in bulk and NZ_M electrons in its d band. Its Fermi energy is E_F and its d atomic level energy E_M. The free atom A has Z_A d electrons having the energy E_A. The overlap integrals corresponding to the metal M are denoted by α and β, and those corresponding to a binding between an atom A and an atom of the metal M by β_{AM}, the change in the α ones being neglected.

We can also define the moments of order n of the density of states of the system, such as M_n being that of the total density of states, m_n that of the density of states normalized to unity, and μ_n the corresponding centered moment.

The two first moments of the density of states of a system, corresponding to three different situations of interest, namely, (a) perfect semi-infinite metal M, (b) adatom M adsorbed on a semi-infinite metal M, and (c) adatom A adsorbed on a semi-infinite metal M, have been calculated using the same technique as described in previous articles.[4,10] They are listed in Table I. The number of first neighbors of a given atom in the metal M is $2\mathfrak{z}$ and $2p$ is the number of added bonds when an atom is adsorbed on M. The constant $C < 1$ depends on the surface crystallography of M. In fact, in the second moment we will neglect the terms in α^2, compared with those in β^2, as the shift of the d band is always much smaller than its width.

Let us now first calculate the binding energy of an atom M on the same metal M. Taking E_M as the zero of energy, $U_B(M-M)$ is simply written as

$$-U_B(M-M) = N\int^{E_{Fb}} E n_{(b)}(E)\,dE - N\int^{E_F} E n_{(a)}(E)\,dE \ , \tag{2}$$

where $n_{(b)}(E)$ and $n_{(a)}(E)$ are, respectively, the density of states corresponding to the situations (b) and (a) (cf. Table I).

This variation of energy is computed using for the density of states Gaussians fitted to their respective first moments[4,8] given in Table I and labeled by (a) or (b) according to the situation of interest. We then get

TABLE I. First moments of the density of states. As we consider differences on energy, the influence of the number of atoms in the surface is of smaller order and can be neglected.

	(a) Perfect semi-infinite metal M	(b) Adatom M on a metal M	(c)[a] Adatom A on a metal M
	$M_0 = 10N$	$M_0 = 10(N+1)$	$M_0 = 10(N+1)$
	$M_1 = 10N(E_M + \alpha)$	$M_1 = 10N(E_M + \alpha) + E_M + \frac{p}{\vartheta}\alpha$	$M_1 = 10N(E_M + \alpha) + E_A + \frac{p}{\vartheta}\alpha$
	$M_2 = 10N(E_M^2 + \alpha^2 + 2E_M\alpha + 2\vartheta\beta^2)$	$M_2 = 10N(E_M^2 + \alpha^2 + 2E_M\alpha + 2\vartheta\beta^2) + 10E_M^2 + 20p\beta^2 + 20E_M\frac{p}{\vartheta}\alpha + 10C\alpha^2$	$M_2 = 10N(E_M^2 + \alpha^2 + 2E_M\alpha + 2\vartheta\beta^2) + E_A^2 + 2p\beta_{AM}^2 + \frac{p}{\vartheta}\alpha(E_A + E_M) + C\alpha^2$
	$m_0 = 1$	$m_0 = 1$	$m_0 = 1$
$m = \frac{M}{10 \times \text{number of atoms}}$	$m_1 = E_M + \alpha$	$m_1 = E_M + \alpha - \frac{1}{N}\left(1 - \frac{p}{\vartheta}\right)\alpha$	$m_1 = E_M + \alpha - \frac{1}{N}(E_M - E_A) - \frac{1}{N} \times \left(1 - \frac{p}{\vartheta}\right)\alpha$
	$m_2 = E_M^2 + \alpha^2 + 2E_M\alpha + 2\vartheta\beta^2$	$m_2 = E_M^2 + \alpha^2 + 2E_M\alpha + 2\vartheta\beta^2 - \frac{1}{N}2\beta^2(\vartheta - p) - \frac{2}{N}E_M\alpha\left(1 - \frac{p}{\vartheta}\right) - \frac{1}{N}\alpha^2(1 - C).$	$m_2 = E_M^2 + \alpha^2 + 2E_M\alpha + 2\vartheta\beta^2 - \frac{1}{N}(E_M^2 - E_A^2) - \frac{2}{N}p(\beta^2 - \beta_{AM}^2) - \frac{2}{N}\beta^2(\vartheta - p) - \frac{2}{N}E_M\alpha\left(1 - \frac{p}{\vartheta}\right) - \frac{1}{N}\frac{p}{\vartheta}\alpha(E_M - E_A) - \frac{1}{N}\alpha^2(1 - C)$
$\mu_0 = m_0$	$\mu_0 = 1$	$\mu_0 = 1$	$\mu_0 = 1$
$\mu_1 = 0$	$\mu_1 = 0$	$\mu_1 = 0$	$\mu_0 = 0$
$\mu_2 = m_2 - m_1^2$	$\mu_2 = 2\vartheta\beta^2$	$\mu_2 = 2\vartheta\beta^2 - \frac{2}{N}(\vartheta - p)\beta^2 + \frac{\alpha^2}{N}\left(C - \frac{p}{\vartheta}\right)$	$\mu_2 = 2\vartheta\beta^2 + \frac{1}{N}(E_M - E_A)^2 + \frac{\alpha}{N} \times (E_M - E_A)\left(1 - \frac{p}{\vartheta}\right) - \frac{2}{N}\beta^2(\ - p) - \frac{2}{N}p(\beta^2 - \beta_{AM}^2) + \frac{\alpha^2}{N}\left(C - \frac{p}{\vartheta}\right)$

[a]The self-consistency is not well treated as we assume that the atom A adsorbed on M has the same energy level as when it is isolated. A discussion of the validity of this approximation will be given later on.

$$U_B(M-M) = 10\left(\frac{\mu_{2a}}{2\pi}\right)^{1/2} e^{-X_F^2/2}\left(1 - \frac{\vartheta - p}{2\vartheta}\right) - Z_M\,\alpha\left(1 - \frac{\vartheta - p}{\vartheta}\right), \quad (3)$$

where

$$X_F = (E_F - m_{1a})/(\mu_{2a})^{1/2},$$

the Fermi level E_F being defined by

$$Z_M = \frac{1}{(2\pi\mu_{2a})^{1/2}}\int^{E_F} \exp\left(-\frac{(E - m_1)^2}{2\mu_{2a}}\right) dE = \frac{1}{(2\pi)^{1/2}}\int_0^{X_F} \exp\left(-\frac{X_F^2}{2}\right) dX .$$

The cohesive energy of the metal M is written in the same approximation as

$$E_c = 10(\mu_{2a}/2\pi)^{1/2} e^{-X_F^2/2} - Z_M\,\alpha;$$

then the binding energy $U_B(M-M)$ can be written as

$$U_B(M-M) = E_c\left(1 - \frac{\vartheta - p}{2\vartheta}\right) + \tfrac{1}{2}Z_M\,\alpha\left(1 - \frac{p}{\vartheta}\right). \quad (4)$$

The overlap integral α is always negative, and therefore $U_B(M-M)$ is always smaller or equal to the cohesive energy of M. The number of added bonds $2p$ depends on the crystallography of the surface of M. $U_B(M-M)$ is equal to E_c when one adds half of the total bonds between nearest neigh-

TABLE II. Relative binding energy of an atom M on the four low index planes of a metal M of structure bcc ($\beta'^2/\beta^2 = 0.25$) and neglecting the shift of the d band ($\alpha = 0$). The correction due to the shift of the d band would be negligible as, for example, taking an upper value of 0.5 eV for tungsten, the correction to the binding energy on a (110) plane of 7 eV would be 0.6 eV, i.e., of the order of a few percent.

Plane	(100)	(110)	(111)	(112)
$\frac{U_B(M-M)}{E_c}$ calc	0.95	0.75	1	0.93
p	4	2	4	3
p'	1	2	3	3

bors ($p = \vartheta$) and in that case one gets the same result as that of a broken-bond model.

It may be reasonably assumed that the overlap integrals between second nearest neighbors are negligible in an fcc structure, as opposed to a bcc structure.[10] In this case, the computation of $U_B(M-M)$ is still straightforward, and labeling by a prime the quantities referring to second nearest neighbors, one has

$$U_B(M-M) = E_c\left(1 - \frac{(\vartheta - p)\beta^2 + (\vartheta' - p')\beta'^2}{2(\vartheta\beta^2 + \vartheta'\beta'^2)}\right) + \tfrac{1}{2} Z_M \alpha\left(1 - \frac{p}{\vartheta}\right) . \quad (5)$$

As has already been emphasized, the integral α is much smaller than the β ones, in particular the contribution of the second neighbors to the shift of the band is negligible. We can therefore neglect them to compute the relative binding energies for various surface crystallograpy for a surface metal of structure bcc or fcc (Tables II and III). The agreement with the experimental results of Plummer and Rhodin is good, as far as the order of magnitude of the binding energy of tungsten on tungsten is concerned, the cohesive energy of tungsten having a value of 8.7 eV, but not as far as the relative magnitude with the index of the surface plane is concerned. One can notice also that our results are similar to those given by a pairwise interaction model, in spite of a complete difference in the assumptions of the calculation.[12] The discrepancies with the experimental values are perhaps due to the various experimental uncertainties[3] which can lead to experimental results for the binding energies which are somewhat controversial. In our model, it can also be due to our neglect of relaxation effects of the surface plane for the adatom. The relaxation effects might be important for example for the (110) and (112) planes, which are possible planes for the stacking faults in bcc crystals.

Let us now calculate the variation of the binding energy $\delta U(M \to A)$ when one replaces the absorption atom M by an adsorbed transition atom A of the same period. This variation $\delta U(M \to A)$ is related to the variation of the total energy δE when one replaces M by A

$$\delta U(M \to A) = -\delta E + (Z_A E_A - Z_M E_M) . \quad (6)$$

If $n_{(b)}(E)$ and $n_{(c)}(E)$ denote, respectively, the density of states of the system, metal M plus adsorbed atom M, and metal M plus adsorbed atom A, corresponding to the moments of the cases (b) and (c) given in Table I, one has

$$\delta E = (N+1)\int^{E_{Fc}} E n_{(c)}(E)\,dE - (N+1)\int^{E_{Fb}} E n_{(b)}(E)\,dE ,$$

$$(N+1) Z_M = (N+1)\int^{E_{Fb}} n_{(b)}(E)\,dE ,$$

$$N Z_M + Z_A = (N+1)\int^{E_{Fc}} n_{(c)}(E)\,dE ,$$

then

$$(N+1)\left[\delta E_F n_{(b)}(E_F) + \int^{E_{Fb}} \delta n(E)\,dE\right] = Z_A - Z_M ,$$

where

$$\delta E_F = E_{Fc} - E_{Fb}, \quad \delta n(E) = n_{(c)}(E) - n_{(b)}(E) .$$

One can then write

$$E = (N+1)\left[\delta E_F E_{Fb} n_{(b)}(E_F) + \int^{E_{Fb}} E \delta n(E)\,dE\right] .$$

Using for the density of states Gaussians fitted to their first moments, as in the computation of $U_B(M-M)$, one gets

$$\delta U(M \to A) = (Z_A - Z_M)(E_A - E_{FM}) + 10\,\frac{(E_A - E_M)^2}{2\mu_{2a}}\left(\frac{\mu_{2a}}{2\pi}\right)^{1/2} e^{-x_F^2/2} + 10p\left(\frac{\mu_{2a}}{2\pi}\right)^{1/2}(\beta_{AM}^2 - \beta^2)\, e^{-x_F^2/2} . \quad (7)$$

If E_c denotes the cohesive energy of the metal M and E_F its Fermi level, the variation of the binding energy when one replaces the adsorbed atom M by A is finally written as

$$\delta U(M \to A) = (Z_A - Z_M)(E_A - E_F) + \frac{E_c + Z_M \alpha}{2\mu_{2a}}$$

TABLE III. Relative binding energy of an atom M on the low index planes of a metal M of structure fcc.

Plane	(100)	(110)	(111)
$\frac{U_B(M-M)}{E_c}$ calc	0.83	0.92	0.75
p	4	5	3

$$\times [(E_A - E_M)^2 + 2p(\beta_{AM}^2 - \beta^2)] \ . \qquad (8)$$

Taking into account also the second nearest neighbors, we have

$$\delta U(M \to A) = (Z_A - Z_M)(E_A - E_F) + \frac{E_c + Z_M \alpha}{2\mu_{2a}}$$

$$\times [(E_A - E_M)^2 + 2p(\beta_{AM}^2 - \beta^2) + 2p'(\beta_{AM}'^2 - \beta'^2)] \ . \qquad (9)$$

The relative variation of the binding energy is given by (9). Following the numerical values of the $5d$ atomic level given in Ref. 13, one can assume that

$$E_A - E_M = -K(Z_A - Z_M) \ ,$$

where K is positive and has a value of 1.3 eV for the $5d$ transition-metal atoms. Equation (9) can then be written as

$$\delta U(M \to A) = -K(Z_A - Z_M)^2 + (Z_A - Z_M)(E_M - E_F) + C[K^2(Z_A - Z_M)^2 + 2p(\beta_{AM}^2 - \beta^2) + 2p'(\beta_{AM}'^2 - \beta'^2)] \ , \qquad (10)$$

with $C = (E_c + Z_M \alpha)/2\mu_{2a}$.

Let us now say some words about the self-consistency problem. Until now we have neglected any charge transfer between the adsorbed atom and the surface metal. Allan and Lenglart[5] have studied this effect in a simplified tight-binding scheme. From their results it can be assumed that the main consequence is to renormalize the atomic level E_A in an effective one E_A^*. One has then to replace (in the crystal), E_A by E_A^* and in the balance in energy one has to subtract $Z_A(E_A^* - E_A) - \frac{1}{2}\delta Z_A(E_A^* - E_A)$. Neglecting the second term, and assuming that $E_A - E_M$ is proportional to $E_A^* - E_M$,[5] that is

$$E_A^* - E_M = \lambda(E_A - E_M) \ ,$$

with $0 \leq \lambda \leq 1$ (from Ref. 5 a reasonable value for λ seems to be 0.5). One has just to replace E_A by E_A^* in Eq. (9) to obtain a better self-consistent variation of binding energy.

Let us now give a numerical computation of the behavior of this variation of the binding energy $\delta U(M \to A)$ for various $5d$ transition metals. For example, for a metal surface of tungsten, one has

$$E_F = E_M + \alpha \ .$$

Neglecting as a first approximation the variation of the β integrals one gets

$$\delta U(M \to A) = (Z_A - Z_M)^2(C\lambda^2K^2 - \lambda K) + \alpha(Z_A - Z_M) \ . \qquad (11)$$

From the experimental value of 8.7 eV of the cohesive energy E_c of tungsten, equal to 10 $\times (\mu_{2a}/2\pi)^{1/2} - Z_M \alpha$, one gets for C a value of 0.9 eV^{-1} if one neglects α, or of 1.0 eV^{-1} taking into account a value of -0.2 eV for α. Taking also a reasonable value of 0.5 for λ, one has for δU

$$\delta U(M \to A) = -(0.25 \text{ eV})(Z_A - Z_M)^2 + \alpha(Z_A - Z_M) \ .$$

The relative binding energy has then a parabolic variation with the variation of charge.

It is rather straightforward to obtain the location of the maximum of the relative binding energy, and one gets

$$\frac{\partial \delta U}{\partial Z_A} = 0 \quad \text{for } Z_A = Z_M - \frac{\alpha}{2(\lambda K - C\lambda^2 K^2)} \ . \qquad (12)$$

The maximum is then always shifted to the right of tungsten by about 0.35.

Let us now estimate the influence of the change in the overlap integrals which is far from being negligible in some cases. Indeed, the overlap integrals β_{AA} are decreasing very sharply for atoms in the series on the right of tungsten.[8]

One can estimate that for an adsorbed atom of rhenium for example, one can take[8] for the difference between transfer overlap integrals of tungsten-tungsten and rhenium-rhenium

$$\beta_{WW} - \beta_{ReRe} \simeq 0.1 \text{ eV} \ ,$$

and for the difference with the mixed transfer overlap integral tungsten-rhenium, an estimated value of half this one:

$$\beta_{WW} - \beta_{ReW} \simeq 0.05 \text{ eV},$$

with

$$\beta_{WW} \simeq 0.75 \text{ eV},$$

so that

$$\beta_{WW}^2 - \beta_{ReW}^2 \simeq 0.07 \text{ eV}^2.$$

For usual surface crystallography, p is equal to 3 or 4, so that $2p(\beta_{ReW}^2 - \beta_{WW}^2) \sim -0.6 \text{ eV}^2$.[14] This term would be then of some importance for the adsorbed atoms on the right of tungsten in the $5d$ series.

The binding energy of the $5d$ transition atoms on a (111) plane of tungsten is shown in Fig. 1. Finally we get for this variation, the following characteristic features: maximum of the order of the cohesive energy of tungsten located between W and Re; parabolic variation with the number of $5d$ electrons with a sharper decrease as the number of $5d$ electrons is increased. These characteristic features are, respectively, mainly due to three different effects, typical surface effect connected with the band structure of the metal, variation of the atomic levels E_A and E_W, and variation of the overlap integrals β.

The general trends of the variation of the binding energy are then roughly similar to the experimental

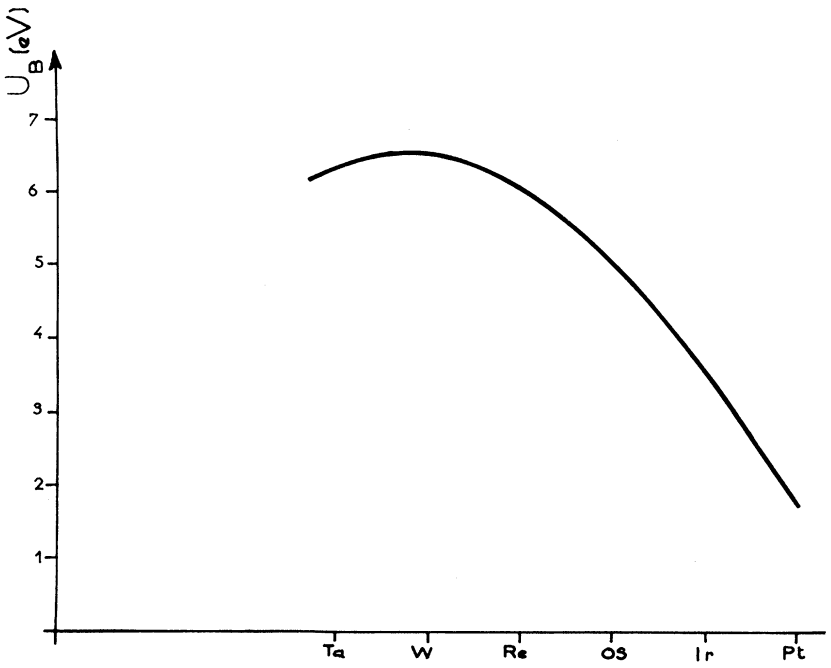

FIG. 2. Theoretical curve for the binding energy of the 5*d* elements on the basal plane of hcp rhenium.

results of Plummer and Rhodin.[1] Nevertheless our calculated curve exhibits a smaller decrease on the left hand of tungsten. The much larger experimental value of the binding energy of rhenium on tungsten compared to tungsten on tungsten receives no convincing explanation in our model.

One can easily compute the binding energy of transition adatoms on other various surface transition metals of 3*d*, 4*d*, or 5*d* series using Eq. (10) and following the same steps as in the computation for tungsten. The main features of the variation of the binding energies with adatom 5*d* electrons are the same for other 5*d* transition-metal substrates as for tungsten. The curve for a substrate of rhenium is shown, for example, in Fig. 2. The maximum of the binding energy given by (4) is of the order of the cohesive energy of rhenium and is located close to tungsten. For other metal surfaces, assuming a reasonable variation for the Fermi energy of substrate, such that

$$E_F - E_M \simeq 0.5(Z_M - 5)\ \text{eV}\ ,$$

we find some similar curves for the variation of binding energy with a maximum always located close to tungsten to its left. The curves have also the same sharp decrease on the right of tungsten due to the variation of the overlap integrals. It would be therefore very interesting to perform experiments similar to those of Plummer and Rhodin on some other substrates to verify the kind of behavior for the binding energies we calculated. Some measurements of the binding energies of 5*d* adatoms on iridium are currently being done by Gallot.

Interaction energies between adatoms could be also easily done using the same technique. These energies are only of some importance for neighboring adatoms. But in any case they are rather small compared to the binding energy of a single adatom, with a maximum of the order of 1 eV. If one builds a whole surface plane of N_s adatoms on a substrate of the same metal, one finds, as it should be, a net gain of energy of $N_s E_c$, where E_c is the cohesive energy of the metal. It seems therefore reasonable that the computation of the binding energy of a single adatom and of the cohesive energy of a bulk metal must be done in the same framework. With this in mind it is not obvious that electron correlation plays the considerable role emphasized by Newns[7] in the binding energy problem, as it is not mainly responsible for the cohesive energy of transition metals.[9,15] This would not be necessarily the case in the general problem of chemisorption.

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[14]One has to notice that this value should be somewhat reduced if we were able to compute the overlap integrals in a self-consistent way.
[15]In his first computation (Ref. 6), using a virtual-bound-state model, Newns has obtained results similar to ours. But this has the same disavantage as his last approach (Ref. 7), as the cohesive energy of bulk transition metal cannot (Ref. 7) be reasonably obtained in this way.

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Generalized Locator–Coherent-Potential Approach to Binary Alloys

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The electronic structure of binary alloys is discussed for a system in which both the atomic energy levels and the hopping integrals are random quantities. This paper is a detailed study of the generalization of the coherent-potential approximation (CPA) introduced earlier by the present authors. We show that a locator description provides a particularly suitable formalism for setting up this generalized problem and how, with the aid of a simple device, configuration averaging may be performed by the use of established techniques. The approximation used is, as in the case of the usual CPA, a single-site one. Three self-consistent equations are obtained that must be solved simultaneously; these replace the single CPA equation. Numerical results are displayed for a series of alloys, and a discussion of certain aspects of the theory, such as its moment-preserving properties, is also included.

I. INTRODUCTION

Much of the work on the electronic theory of binary alloys has been a development of the multiple-scattering formalism of Lax.[1] At present a rather satisfying stage in the theory seems to have been reached with the introduction of the coherent-potential approximation (CPA) by Soven,[2] and its subsequent developments.[3,4] The simplicity of the CPA arises from the fact that formally it can be viewed as a reduction of the alloy problem to one of a single impurity in a self-consistently determined effective lattice. In the usual tight-binding model, only the atomic energy levels are assumed to be random, i.e., to depend on the occupation of sites by either of the constituent species. In the effective-medium approach one replaces the averaged alloy by a periodic lattice of "effective atoms," whose effective localized energy is to be determined, and whose coupling (via hopping integrals) is the same as in the real alloy. One now introduces a single real atom into the effective lattice (this replacement, it is assumed, does not affect the coupling, but has only the effect of producing a perturbation localized on the impurity site itself) and determines the condition that on the average (the impurity can be either of two species) no scattering occurs, i.e., the average single-site t matrix is zero. This gives the CPA self-consistency condition.

The introduction of this effective lattice simplifies the derivation of the self-consistency equation, but it is not essential. For example, we can use, if we wish, the virtual crystal—or indeed the pure lattice of either of the constituent atomic species—as the "unperturbed" lattice, and then perform the more complicated multiple-scattering calculation. The difficulty then arises of dealing with multiple-occupancy effects correctly. This has been done by Leath,[5] among others. Using a diagrammatic propagator expansion technique, Leath shows how to sum all non-crossed-line diagrams in the perturbation series. Since such diagrams have a single-site nature, their summation