PHYSICAL REVIEW B VOLUME 30, NUMBER 8 15 OCTOBER 1984

Comments

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Comment on "Universal features of bonding in metals"

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(Received 23 December 1983; revised manuscript received 31 May 1984)

Using a very simple model, valid for transition metals, we derive binding-energy–distance universal relations. We compare our results with those obtained by Rose, Smith, Ferrante, and Guinea.

I. INTRODUCTION

There has been recently a revival of interest concerning the universal features of bonding in metals.[1-7] In particular Rose, Ferrante, and Smith[2] (hereafter referred to as RFS) have shown that theoretical binding-energy–distance curves can be approximately scaled into a single universal relation in each of the following cases: chemisorption on a metal surface, surface and adhesion energies, and cohesion of a bulk metal. In each case the energy relation can be expressed as

$$\frac{E(a)}{\Delta E}=E^*(a^*) \ , \tag{1.1}$$

where $E(a)$ is the total energy per atom as a function of the interatomic distance a and ΔE its absolute value at the equilibrium separation a_m. The coordinate a^* is a scaled length defined by

$$a^*=(a-a_m)/l \ . \tag{1.2}$$

l is a scaling length which is to be determined. $E^*(a^*)$ is an approximately universal function which describes the shape of the binding-energy curve.

The scaling parameter ΔE and the translation $(a-a_m)$ ensure that all the curves will go through the point of coordinates $(a^*=0,\ E^*=-1)$ at their minimum. The choice of l is less obvious, and in a first step RFS identify l with the Thomas Fermi screening length l_{TF}. With this definition of l, the universality of atomic binding-energy curves is well obeyed separately for chemisorption on jellium surfaces and surface and adhesive energies of simple metals. However, the scaled bulk cohesive energy as a function of $(r_{\mathrm{WS}}-r_{\mathrm{WS}_m})/l_{\mathrm{TF}}$ [$r_{\mathrm{WS}_{(m)}}$ is the (equilibrium) Wigner-Seitz radius] exhibits some deviations from universality. For this reason, and also in the hope of extending the universal relation to diatomic molecules, RFS introduce a new scaling length l by requiring that the second derivative of the total energy with respect to atomic separation at equilibrium is equal to unity. With this new scaling length, the universality of the bulk cohesive energy-distance curves becomes much better and all universal relations fall on top of each other. This is not really surprising around the bottom of the potential well since with this choice of scaling parameters all the scaled energy-distance curves are forced to go through the same minimum point $(a^*=0,\ E^*=-1)$ with a curvature equal to unity. Therefore, around the minimum point these curves can only differ by a term of the order of $(a^*)^3$. But the surprise comes from the fact that this universal relation still holds at distances where the third-order term becomes important.

As a consequence of this universality RFS relate seemingly different physical quantities: cohesive and surface energies, vibration stretch frequency, and binding energy of adsorbates.

In this paper we will focus on transition metals and show how universal analytic energy-distance curves can be derived from a simple tight-binding model. From this model we relate easily the above mentioned physical quantities.

II. MODEL

We neglect the electronic correlation energy and assume for simplicity that, due to symmetry, all bonds are equivalent. The energy distance contains two contributions:

$$E=E_{\mathrm{rep}}+E_{\mathrm{band}} \ .$$

E_{rep} is a repulsive contribution to the energy which will be assumed to be pairwise and described by a potential of the Born-Mayer type (exponentially decreasing with distance). E_{band} is the one-electron contribution. In a tight-binding model, it increases with the hopping integrals which are assumed to vary exponentially with distance as $\exp(-qR)$. These exponential laws are derived from a fit to microscopic calculations and are valid over a relatively large domain of distances around the equilibrium position.[8,9]

A. Bulk energies

The one-electron contribution to the bulk energy per atom can be written

$$E_{\text{band}} = \int_{m}^{E_F} E n(E)\,dE \;, \tag{2.1}$$

where $n(E)$ is the centered density of states, m the bottom of the band, and E_F the Fermi level. When $n(E)$ is approximated by a Gaussian of width fitted to the second moment of the true density of states, it is well known[10,11] that E_{band} takes the form

$$E_{\text{band}} = -\sqrt{Z} F e^{-qR} \;, \tag{2.2}$$

where Z is the coordination number of a bulk atom, R the interatomic spacing, and F a function independent of R $(F>0)$. One sees that this term is not pairwise since it varies like $\sqrt{Z}$. Furthermore, let us notice that this $\sqrt{Z}$ dependence would also be obtained with parabolic or rectangular densities of states and is approximately obeyed when using accurate densities of states.

Consequently, the bulk energy per atom $E_b(R)$ at interatomic distance R takes the following form:

$$E_b(R) = \frac{ZA}{2} e^{-pR} - \sqrt{Z} F e^{-qR} \;, \tag{2.3}$$

where Ae^{-pR} $(A>0)$ is the repulsive energy associated to one bond. The existence of a minimum for E_b requires $p>q$ and the equilibrium distance satisfies

$$p\frac{ZA}{2} e^{-pR_0} = qF\sqrt{Z} e^{-qR_0} \;, \tag{2.4}$$

which corresponds to the cohesive energy

$$E_b(R_0) = \frac{ZA}{2} e^{-pR_0}\left(1-\frac{p}{q}\right) = F\sqrt{Z} e^{-qR_0}\left(\frac{q}{p}-1\right) \;. \tag{2.5}$$

When we scale (2.3) by (2.5) we find

$$E_b^*(R) = \frac{E_b(R)}{|E_b(R_0)|} = \frac{e^{-p(R-R_0)}}{(p/q)-1} + \frac{e^{-q(R-R_0)}}{(q/p)-1} \;. \tag{2.6}$$

Let us calculate now the scaling length l by requiring that the curvature of $E_b^*(R^*)$ is equal to 1 at the minimum

$$\left[\frac{d^2E^*(R)}{dR^2}\right]_{R=R_0} = \frac{1}{l^2} = pq \;. \tag{2.7}$$

Therefore,

$$E_b^*(R^*) = \frac{e^{-(p/q)^{1/2}R^*}}{(p/q)-1} + \frac{e^{-(q/p)^{1/2}R^*}}{(q/p)-1} \;, \tag{2.8}$$

where

$$R^* = \frac{R-R_0}{l} \;. \tag{2.9}$$

The potential given by expression (2.8) is strictly universal provided that the ratio p/q is constant along the transition-metal series which is roughly true since, from an analysis of the cohesive energy and elastic constants, Ducastelle[12] has shown that $3 \lesssim p/q \lesssim 5$. Moreover, if we vary p/q within realistic limits (from 2 to 5) the scaled energy-distance curves are almost indistinguishable at small R^* distances and do not differ very much at large R^*, as can be seen on Fig. 1. The value $p/q=2$ corresponds to the Morse potential, as can be seen on Eq. (2.6). However, if we limit ourselves to first nearest neighbors, this value of p/q leads to vanishing values of the shear moduli.[12] It is, thus, not appropriate for transition metals.

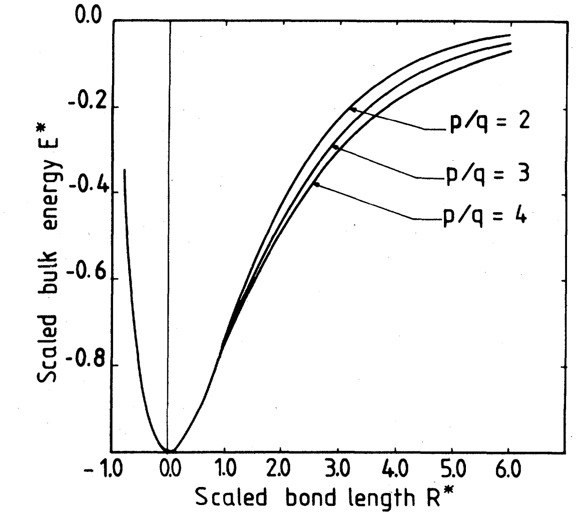

FIG. 1. Scaled bulk cohesive energy-distance curves for different values of p/q.

When the separation between atoms is characterized by the Wigner-Seitz radius as in the work of RFS Eq. (2.8) is unchanged but the scaling length becomes

$$l_b = \frac{1}{\lambda\sqrt{pq}} \;, \tag{2.10}$$

where

$$\lambda = \frac{R_0}{r_{\text{WS}_m}} \;;$$

i.e.,

$$\lambda = \frac{1}{\sqrt{2}}\left(\frac{16\pi}{3}\right)^{1/3} = 1.81$$

for the fcc structure, and

$$\lambda = \frac{\sqrt{3}}{2}\left(\frac{8\pi}{3}\right)^{1/3} = 1.76$$

for the bcc structure.

In Ref. 4 Rose, Smith, Guinea, and Ferrante propose to approximate $E^*(a^*)$ using the function

$$E^*(a^*) = -[1+a^*+0.05(a^*)^3]e^{-a^*} \;. \tag{2.11}$$

By definition, when $R^*=0$ $(a^*=0)$ both functions go through the point $E^*=-1$ and their first and second derivatives have the same values equal, respectively, to 0 and 1. It is, thus, possible to determine the p/q ratio to get the same third derivative. This gives

$$p/q = 2.95 \;. \tag{2.12}$$

With this value the fourth derivatives differ by only 2%. In fact, the corresponding curves are almost undiscernible. Equation (2.12) lies within the estimations of Ducastelle[12] ($qR_0=3$ and $pR_0=9$–15) in transition metals. It leads to

$$l_b \simeq \frac{R_0}{10} \tag{2.13}$$

for all structures in good agreement with RFS evaluations from experimental data.

On the other hand, one can also compute the position of

TABLE I. Variation of pR_0 and qR_0 along the three transition-metal series deduced from Eqs. (2.12) and (2.15); the η value is taken from Rose *et al.* (Ref. 4).

	Ti	V	Cr	Mn	Fe	Co	Ni
η	4.76	4.81	5.59		5.16	5.31	5.11
pR_0	8.18	8.40	9.60		8.86	9.12	8.78
qR_0	2.77	2.85	3.25		3.00	3.09	2.98

	Zr	Nb	Mo	Tc	Ru	Rh	Pd
η	4.48	4.84	5.85		6.04		6.41
pR_0	7.69	8.31	10.05		10.37		11.01
qR_0	2.61	2.82	3.41		3.52		3.73

	Hf	Ta	W	Re	Os	Ir	Pt
η	4.66	4.92	5.69	6.15		6.52	6.47
pR_0	8.00	8.45	9.77	10.56		11.20	11.11
qR_0	2.71	2.86	3.31	3.58		3.80	3.77

the inflection point in (2.8). It lies at

$$R^* = \frac{(p/q)^{1/2}\ln(p/q)}{(p/q)-1} \; ; \tag{2.14}$$

i.e., $R^* = 0.95$, 0.92, and 0.90 when $p/q = 2.95$, 4, and 5, respectively, which compares quite well with the relation $(r_{\rm WS} - r_{{\rm WS}_m}) \simeq l_b$ given by Guinea, Rose, Smith, and Ferrante.[3]

The η parameter $(\eta = r_{{\rm WS}_m}/l_b)$ tabulated by Rose *et al.*[4] for all transition elements has the expression in our model

$$\eta = R_0\sqrt{pq} \;\; , \tag{2.15}$$

which, with (2.12), can be used to derive pR_0 and qR_0. They are given in Table I. One sees that they increase along a transition series.

Finally Guinea *et al.*[3] relate the Grüneisen parameter which controls the anharmonic properties of bulk metals to η:

$$\gamma = \frac{1}{6}\frac{r_{{\rm WS}_m}}{l_b}\frac{E^{*\prime\prime\prime}(a)}{E^{*\prime\prime}(a)} = 0.38\eta \;\; . \tag{2.16}$$

With our model we find

$$\gamma = \frac{(p/q)+1}{6(p/q)^{1/2}}\eta \;\; . \tag{2.17}$$

The proportionality factor between γ and η takes the values 0.38, 0.41, and 0.45 for $p/q = 2.95$, 4, and 5, respectively.

B. Binding energies of adatoms

We have already shown that this model can be applied in chemisorption in the case of weak (or intermediate) coupling[11] for which the perturbation of the substrate can be neglected. In this case the binding energy takes a form identical to Eq. (2.3):

$$E = ZAe^{-pR} - \sqrt{Z}Fe^{-qR} \;\; , \tag{2.18}$$

where Z is the coordination number of the adsorbate; A, p, and q characterize the adatom-substrate bond and R is the bond length. This equation leads obviously to the same scaled binding-energy–bond-length curve [Eq. (2.8)] with the same expression of the scaling length. This curve is universal in so far as p/q is constant.

If, similarly to RFS, we replace the bond length by the distance a of the adatom to the surface, R should be expressed as a function of a, which leads to a more complicated form of the universal relation, and the scaling length becomes

$$l_{\rm chem} = \frac{1}{\sqrt{pq}\,\cos\theta_0} \;\; , \tag{2.19}$$

where θ_0 is the angle of the bond with the normal to the surface at equilibrium.

C. Surface energies

For the sake of simplicity we will only consider here the most densely packed faces of each metal, in which case, within our model, the variation of total energy when separating two semi-infinite portions of a metal is only due to the perturbation of the surface atoms. If the bond length between the two half-crystals is equal to R, this variation of energy, per surface atom, takes the form

$$\Delta E = E(R) - E(\infty) \;\; , \tag{2.20}$$

where

$$E(R) = \frac{Z-Z_c}{2}Ae^{-pR_0} + \frac{Z_cA}{2}e^{-pR} - F[(Z-Z_c)e^{-2qR_0} + Z_ce^{-2qR}]^{1/2} \tag{2.21}$$

and Z_c is the number of broken bonds.

To obtain a simple form of the potential we expand the square root in (2.21) up to the second order in Z_c/Z. We find

$$\frac{\Delta E(R^*)}{|\Delta E(R_0)|} = \frac{1}{(p/2q)(1+\alpha)-1}\left[e^{-plR^*} - \frac{p}{2q}(1+2\alpha)e^{-2qlR^*} + \frac{p\alpha}{2q}e^{-4qlR^*}\right] \;\; , \tag{2.22a}$$

where

$$|\Delta E(R_0)| = \frac{Z_c A e^{-pR_0}}{2}\left[\frac{p}{2q}(1+\alpha)-1\right] \tag{2.22b}$$

is the surface energy and l is the scaling length given by

$$l=\left[|\Delta E(R_0)|\left(\frac{d^2E(R)}{dR^2}\right)^{-1}_{R=R_0}\right]^{1/2}$$

$$=\left[\frac{p(1+\alpha)-2q}{2pq[p+2q(2\alpha-1)]}\right]^{1/2}, \tag{2.23}$$

with $\alpha = Z_c/4Z$. Expression (2.22a) is identical to (2.8) when $p=2q$ and for realistic values of p/q, the two potentials do not differ very much over a wide variation of R^* around 0 (Fig. 2). Let us notice that we do not take into account the relaxation of the interplanar spacings near the cleavage plane.

To compare the scaling length (l_s) of RFS and ours, we must replace R by the distance a between the two half-crystals; then l is divided by $\cos\theta_0$. If, for example, we take a (111) fcc surface $\cos\theta_0=\sqrt{2/3}$, $\alpha=\frac{1}{16}$ one finds

$$\frac{l_b}{l_s}=0.65,\ 0.64,\ \text{and}\ 0.62$$

when

$$\frac{p}{q}=2.95,\ 4,\ \text{and}\ 5\ . \tag{2.24}$$

These values are a bit larger than those of RFS and we will discuss this in Sec. III. Let us point out that, since $0<\alpha<\frac{1}{8}$, l is almost independent of α for reasonable values of p/q.

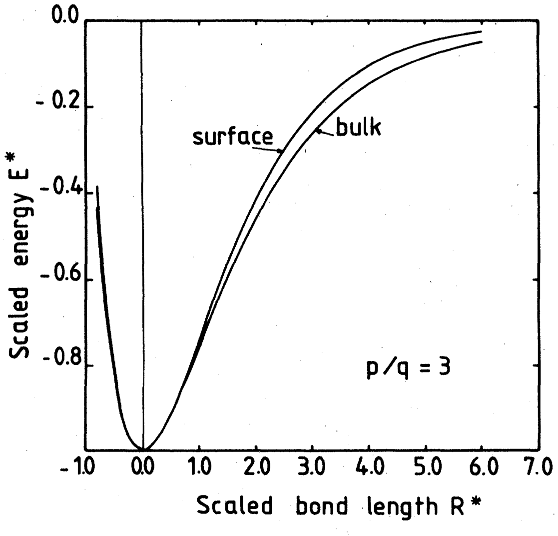

FIG. 2. Scaled surface energy-distance curve compared with the scaled bulk cohesive energy-distance curve: $p/q=3$ and $\alpha=\frac{1}{16}$ [(111) face of a fcc metal].

III. DISCUSSION AND CONSEQUENCES

Let us first discuss the ratio l_b/l_s. RFS estimates it from measured quantities using the expressions

$$l_s=\left[\frac{2\sigma d}{c'_{11}}\right]^{1/2}, \tag{3.1a}$$

$$l_b=\left[\frac{|E_b(R_0)|}{12\pi B r_{\mathrm{ws}_m}}\right]^{1/2}, \tag{3.1b}$$

where σ is the surface energy per unit area, c'_{11} the elastic constant appropriate to strain normal to the surface, d the interplanar separation at equilibrium, and B the bulk modulus.

The above expression of l_b is identical to (2.10) since it is easy to show that[12]

$$B=\frac{1}{12\pi r_{\mathrm{ws}_m}}\lambda^2 pq|E_b(R_0)|\ . \tag{3.2}$$

The expression of l_s, as stated by RFS, is only approximate since the appropriate elastic constant $c_\perp$ for the separation into two-half crystals is not the same as c'_{11}, which corresponds to a uniform variation of all interplanar distances.

Indeed, within our model, $c_\perp$ can be easily obtained from the second derivative of $E(R)$ given by Eq. (2.21). We find

$$c_\perp=\frac{1}{v_{at}}p^2Ae^{-pR_0}Z_c\left[1-2\frac{q}{p}\left(1-\frac{Z_c}{2Z}\right)\right]d^2\cos^2\theta_0\ , \tag{3.3}$$

where d is the interplanar distance at equilibrium and v_{at} the atomic volume. The expression of c'_{11} can be similarly derived from (2.21) but one should replace Z_c by $2Z_c$ since the interplane bond lengths on both sides of a given plane are modified. This gives

$$c'_{11}=\frac{1}{v_{at}}p^2Ae^{-pR_0}Z_c\left[1-2\frac{q}{p}\left(1-\frac{Z_c}{Z}\right)\right]d^2\cos^2\theta_0\ . \tag{3.4}$$

Expressions (3.3) and (3.4) are identical only if we limit ourselves to the first order in Z_c/Z. Using this assumption one recovers the expression (3.1a) of the surface scaling length. However, higher-order terms in Z_c/Z are actually necessary to recover the usual relations between c'_{11} and c_{11}, c_{12}, and c_{44} in cubic crystals and, therefore, Eq. (3.1a) is not strictly valid. If, nevertheless, we limit ourselves to first order in Z_c/Z for the expressions of c'_{11} and σ and apply Eqs. (3.1) we find

$$\frac{l_b}{l_s}=\frac{\sqrt{2}\cos\theta_0}{\lambda}\ ; \tag{3.5}$$

i.e., for a (111) fcc surface $l_b/l_s=0.63$, which is quite similar to (2.24).

The difference between our value of l_b/l_s and the value (0.48 ± 10%) quoted by RFS is partly due to the fact that our simple model seems to underestimate somewhat the surface energy while RFS use a slightly overestimated σ since these quantities are taken from measurements on polycrystals.

Within our model, we can also calculate the ratio

TABLE II. Comparison of ratios of adsorbate-substrate vibrational stretch mode frequency computed from Eq. (3.10) with those of Ref. 13 for N, O, and F atoms adsorbed on the (110) face of bcc transition metals with N_d d electrons. B_1 is the bridge site between nearest neighbors and T_D the most stable adsorption site (almost perfect ternary).

			$\omega_{B_1}/\omega_{T_D}$	
		$N_d=3$	$N_d=5$	$N_d=7$
N	Ref. 13	1.10	1.14	1.15
	Eq. (3.10)	1.12	1.13	1.13
O	Ref. 13	1.10	1.09	1.12
	Eq. (3.10)	1.11	1.05	1.10
F	Ref. 13	1.03	1.07	1.07
	Eq. (3.10)	1.08	1.04	1.09

$\sigma/|E_b(R_0)|$ from Eqs. (2.5) and (2.22b). We find

$$\frac{\sigma}{|E_b(R_0)|}=\frac{1}{S}\frac{Z_c}{Z}\frac{(p/2q)(1+\alpha)-1}{(p/q)-1}\ , \tag{3.6}$$

where S is the surface area per surface atom.

Let us now compute $\mu=4\pi r_{\mathrm{WS}_m}^2\sigma/|E_b(R_0)|$ for specific surfaces in order to compare this ratio to the values derived from Eqs. (3.5) and (6.1) of RFS. For the (111) and (100) faces of a fcc crystal, we obtain μ equal, respectively, to 0.32, 0.42, 0.46, and 0.39, 0.50, 0.55, when $p=2.95q$, $4q$, $5q$. These values roughly agree with Eq. (3.5) of RFS, which gives $\mu\simeq 0.33$ but is too small by a factor of approximately 2 compared to the empirical result (0.82) given by their Eq. (6.1). Let us notice, however, that according to RFS this last value is strictly given with an uncertainty of ±40%, although the straggling of the experimental values in the plot of their Fig. 13 is much smaller, which indicates some compensation between errors. The discrepancy between our values and the empirical estimation of RFS (0.82) is mainly due to the difference between our value of l_b/l_s and theirs, since we agree with the RFS evaluation of c_{11}'/B as we will show below.

Indeed, for the (111) face of a fcc crystal, (3.4) gives

$$c_{11}'=\frac{2}{3v_{at}}Ae^{-pR_0}(pR_0)^2\left(2-3\frac{q}{p}\right) \tag{3.7}$$

and[12]

$$B=\frac{c_{11}+2c_{12}}{3}=\frac{2}{3v_{at}}Ae^{-pR_0}(pR_0)^2\left(1-\frac{q}{p}\right)\ .$$

This gives

$$\frac{c_{11}'}{B}=\frac{2-3(q/p)}{1-(q/p)}\ ; \tag{3.8}$$

i.e., $c_{11}'/B=1.49$, 1.67, 1.75 when $p=2.95q$, $4q$, $5q$. A similar calculation leads to $c_{11}'/B=1.24$, 1.33, 1.38 for a (100) face. These values are in reasonable agreement with the value (1.7 ±20%) used by RFS.

Finally, we can compute the ratio of vibrational stretch frequencies for different atomic adsorbates ignoring modes in which the vibration of the substrate atoms is important. The force constant is simply given by

$$k=\left(\frac{d^2E(R)}{dR^2}\right)_{R=R_0}=\frac{E(R_0)}{l_{\mathrm{chem}}^2}\ . \tag{3.9}$$

Therefore,

$$\frac{\omega_2}{\omega_1}=\left(\frac{E_2(R_{0_2})M_1p_2q_2}{E_1(R_{0_1})M_2p_1q_1}\right)^{1/2}\frac{\cos\theta_2}{\cos\theta_1}\ , \tag{3.10}$$

where ω_i is the vibrational stretch frequency of an adatom i, $E_i(R_{0_i})$ its energy at the equilibrium bond length R_{0i}, M_i its mass, and θ_i is the angle of the adatom-substrate bonds with the normal to the surface. Equation (3.10) is, thus, similar to Eq. (3.8) of RFS. Although in our work it is derived under the assumption of weak or intermediate coupling one can wonder about its reliability in the strong-coupling limit. In order to check it, we will consider the case of an atom (N, O, or F) at a bridge position between nearest neighbors (site B_1 of Ref. 13) and at a nearly ternary site (site T_D of Ref. 13) adsorbed on a (110) face of a bcc transition metal. In this geometry the adatom-substrate bonds are almost equivalent, which is indeed an essential assumption in Eq. (2.18). We have computed the ratio $\omega_{B_1}/\omega_{T_D}$ from Eq. (3.10) and compared it to the results of our previous calculations[13] using a more sophisticated tight-binding model. The agreement is rather good, as can be seen in Table II. Note that the site dependence of the vibration frequency of adatoms has been discussed in great length by Sayers[14] using an expression for the chemisorption energy similar to Eq. (2.18).

IV. CONCLUSION

In conclusion, we have set up a very simple model, valid for transition metals, which gives a physical insight into the universal nature of binding-energy–distance relations. Our model reproduces the relations put forward by RFS and Guinea *et al.*[3] and gives a means to determine *a priori* the constant factors which appear in them.

ACKNOWLEDGMENTS

We are grateful to Dr. Tréglia and Dr. Ducastelle for extensive discussions and a critical reading of the manuscript.

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[1] J. H. Rose, J. Ferrante, and J. R. Smith, Phys. Rev. Lett. **47**, 675 (1981); J. R. Smith, J. Ferrante, and J. H. Rose, Phys. Rev. B **25**, 1419 (1982); J. Ferrante, J. R. Smith, and J. H. Rose, Phys. Rev. Lett. **50**, 1385 (1983).

[2] J. H. Rose, J. R. Smith, and J. Ferrante, Phys. Rev. B **28**, 1835 (1983).

[3] F. Guinea, J. H. Rose, J. R. Smith, and J. Ferrante, Appl. Phys. Lett. **44**, 53 (1984).

[4] J. H. Rose, J. R. Smith, F. Guinea, and J. Ferrante, Phys. Rev. B **29**, 2963 (1984).

[5] E. Zaremba, Solid St. Commun. **23**, 347 (1977).

[6] W. Kohn and A. Yaniv, Phys. Rev. B **20**, 4948 (1979).

[7] G. Vidali, M. W. Cole, and J. R. Klein, Phys. Rev. B **28**, 3064 (1983).

[8] L. W. Anders, R. S. Hansen, and L. S. Bartell, J. Chem. Phys. **59**, 5277 (1973).

[9] Y. Boudeville, J. Rousseau-Violet, F. Cyrot-Lackmann, and S. N. Khanna, J. Phys. (Paris) **44**, 433 (1983).

[10] G. Allan, in *Handbook of Surfaces and Interfaces,* edited by L. Dobrzynski (Garland STPM, New York, 1978), and references therein.

[11] M. C. Desjonquères and D. Spanjaard, J. Phys. C **15**, 4007 (1982).

[12] F. Ducastelle, J. Phys. (Paris) **31**, 1055 (1970).

[13] M. C. Desjonquères and D. Spanjaard, J. Phys. C **16**, 3389 (1983).

[14] C. M. Sayers, J. Phys. C **12**, 4333 (1979); Surf. Sci. **99**, 471 (1980).