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Energetics of charged metallic particles: From atom to bulk solid

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The energy of a spherical metallic particle of radius R, charged with Z excess electrons, is simply $E_Z = E_0 - ZW + Z^2e^2/2(R+a)$, where W is the bulk work function, e is the charge of one electron, and $R+a$ is the radial centroid of the excess charge. Consequently, the ionization energy is $I = W + e^2/2(R+a)$, and the electron affinity is $A = W - e^2/2(R+a)$. These formulas apply even to the smallest microparticle, a single monovalent atom. Thus they may be used to estimate the bulk work function $W = (I+A)/2$ and density parameter (Wigner-Seitz radius) r_s from atomic values for I and A; r_s is the solution of the equation $r_s + a(r_s) = e^2/(I-A)$. The link between microcosm and macrocosm is further shown by the relationship $\varepsilon_{\mathrm{coh}} \approx \sigma 4\pi r_s^2$ between the cohesive energy $\varepsilon_{\mathrm{coh}}$ and the surface tension σ. These relationships are illustrated for atoms and small jellium spheres.

I. INTRODUCTION AND SUMMARY

Small metallic particles[1,2] mediate between single monovalent atoms and bulk metals. Clusters of special stability occur with 8, 20, 40, 58, and 92 atoms.[3] These magic numbers are shell-closing numbers of a spherical square-well potential confining the valence electrons inside the particle. The jellium (uniform positive background) model of the bulk metal provides a useful zeroth-order approximation for alkali-metal crystals[4] and planar surfaces,[5] and the jellium-sphere model does the same for alkali-metal particles.[6–13] Starting from this model, and introducing the ionic pseudopotentials as a first-order perturbation, one can calculate the total energy, the ionization energy and electron affinity, and even the atomic arrangements in space, which often differ radically from those of the bulk crystal. The results are generally confirmed by much more elaborate calculations of the molecular-structure type.[11,14] A particularly cogent explanation of the physics behind the success of the jellium-sphere model has been given by Manninen.[11]

Of special interest is the question: How do the properties of a particle converge, as a function of cluster size, from those of a single atom to those of a bulk crystal? Because of its high symmetry, the jellium-sphere model converges via a strong shell-structure oscillation[9] which is partially damped when the ionic pseudopotentials are switched on. It has been suggested that, apart from shell-structure oscillations, the ionization energy I and electron affinity A of a particle of radius R should converge toward the work function W of the bulk crystal in the following way:[15–17]

$$I = W + 3e^2/8R \ , \tag{1}$$

$$A = W - 5e^2/8R \ . \tag{2}$$

These equations, or a variant[6,18] replacing $+\frac{3}{8}$ and $-\frac{5}{8}$ by $+\frac{1}{2}$ and $-\frac{1}{2}$, are often used to provide an elementary tual interpretation of the results of experiments or detailed calculations. It will be shown here (Sec. II A) that the more correct equations are

$$I = W + e^2/2(R+a) \ , \tag{3}$$

$$A = W - e^2/2(R+a) \ , \tag{4}$$

where $R+a$ is the radial centroid of excess charge[19] on a metallic sphere of radius R. Apart from shell-structure oscillations,[20] the microscopic distance a depends upon the interior density of the particle, but is almost independent of the radius R.[21] Charging always raises the electrostatic energy of a neutral system; this effect increases I (the energy needed to transform the neutral atom into the positive ion), and reduces A (the energy needed to transform the negative ion into the neutral atom).

Equations (3) and (4) apply with reasonable accuracy even to very small particles, including the smallest—a jellium sphere containing a single electron, or a real monovalent atom (Sec. II B). The upshot is an unexpected link [Eqs. (17) and (19)] between the ionization energy and electron affinity of an atom, on the one hand, and the work function and bulk density of the corresponding metal, on the other.

The revised equations (3) and (4) have some implications for the equilibrium charge and stability of a cluster (Sec. II C). In a collection of particles of varying size but identical composition at absolute zero temperature, there is always a range of chemical potentials which will make every particle neutral, contrary to the tentative suggestion of van Staveren *et al.*[17] based upon Eqs. (1) and (2). However, Ishii's observation[22] remains true: the smallest number of atoms in a cluster that can bind Z excess electron increases very rapidly with Z.

A second close and simple line between microcosm and macrocosm is provided by the relationship of Eq. (26) between cohesive energy and surface tension (Sec. III). Apparently, for many purposes, a monovalent atom may be regarded as a small metallic particle or even as a jellium sphere. Similarly, a nucleon may be regarded as a small sphere of nuclear matter.

II. IONIZATION ENERGY AND ELECTRON AFFINITY

A. Spherical metallic particles

Let the bulk metal have work function W (binding energy of the least-bound electron) and an average valence electron density $\bar{n}=3/4\pi r_s^3$. Consider a spherical particle which when neutral would contain N^* valence electrons; the radius of its Gibbs surface is thus $R=r_s(N^*)^{1/3}$. The problem is to determine how the energy of such a particle, with N^*+Z valence electrons, depends upon Z. Here N^* and Z are integers. The shell-structure effects present in very small particles are to be neglected.

Let

$$\delta n(\mathbf{r})=Zf(r)/4\pi(R+a)^2 \tag{5}$$

be the excess electron density. Because metal is a conductor, the function $f(r)$ is nonzero only in a peak[19] near the surface of the particle. Neglecting shell structure, the height and width of this peak are independent[21] of R, and

$$\int_0^\infty dr\, 4\pi r^2[f(r)]/4\pi(R+a)^2=1 \;, \tag{6}$$

$$\int_0^\infty dr\, 4\pi r^2 r[f(r)]/4\pi(R+a)^2=(R+a) \;. \tag{7}$$

The parameter a is just the microscopic distance from the infinite planar Gibbs surface to its image plane, as first calculated for the jellium model within the local-density approximation by Lang and Kohn.[19] Those calculations have been repeated here, and the results in the metallic range $2\le r_s\le 6$ have been fitted:

$$a(r_s)=5.207r_s^{-3/2}-7.415r_s^{-1}+4.874r_s^{-1/2} \tag{8}$$

(all distances in bohrs).

The energy E of the particle is[23] a functional of its electron density $n(\mathbf{r})$. The charging energy may be expanded to order Z^2:

$$E[n+\delta n]-E[n]=\int d^3r \left.\frac{\delta E}{\delta n(\mathbf{r})}\right|_{N^*}\delta n(\mathbf{r}) +\frac{1}{2}\int d^3r\int d^3r' \left.\frac{\delta^2 E}{\delta n(\mathbf{r})\delta n(\mathbf{r}')}\right|_{N^*} \times\delta n(\mathbf{r})\delta n(\mathbf{r}') \;. \tag{9}$$

Again neglecting shell structure, the functional derivatives will exist; derivative discontinuities[24] need not be considered here.

The total energy $E[n]$ is the sum of the electrostatic energy

$$E_{\mathrm{es}}[n]=\frac{1}{2}\int d^3r\int d^3r' \frac{[n(\mathbf{r})-n_+(\mathbf{r})][n(\mathbf{r}')-n_+(\mathbf{r}')]}{|\mathbf{r}'-\mathbf{r}|} \;, \tag{10}$$

the kinetic energy $T_s[n]$, and the exchange-correlation energy $E_{\mathrm{xc}}[n]$. In Eq. (10), $n_+(\mathbf{r})$ is the density of the positive charge, which arises either from the nuclei in a real particle or from the uniform positive background inside the Gibbs surface in a jellium model. The required functional derivatives of Eq. (10) are

$$\frac{\delta E_{\mathrm{es}}}{\delta n(\mathbf{r})}=\int d^3r' \frac{[n(\mathbf{r}')-n_+(\mathbf{r}')]}{|\mathbf{r}'-\mathbf{r}|} \;, \tag{11}$$

$$\frac{\delta^2 E_{\mathrm{es}}}{\delta n(\mathbf{r})\delta n(\mathbf{r}')}=\frac{1}{|\mathbf{r}'-\mathbf{r}|} \;. \tag{12}$$

Neglecting shell-structure effects, there will be no important R dependence in the first term on the right-hand side of Eq. (9), which may therefore be replaced by its bulk ($R\rightarrow\infty$) limit, $-WZ$. The second term on the right-hand side of Eq. (9) contains an electrostatic term $Z^2e^2/2(R+a)$. The kinetic and exchange-correlation energies can make no comparable contribution. For example, if the exchange-correlation energy is treated in the local-density approximation,[25] its contribution of order Z^2 will be

$$\frac{1}{2}\int_0^\infty dr\, 4\pi r^2 g(n(r))[Zf(r)/4\pi(R+a)^2]^2 \;, \tag{13}$$

TABLE I. Test of Eq. (16) for jellium spheres with electron number $N^*=1$ and radius $R=r_s$. I is the exact ionization energy, and r_s is the bulk density parameter. $a(r_s)$ is the distance from the Gibbs surface to the image surface [Eq. (8)], and W is the work function of a planar surface, calculated self-consistently within the local-density approximation for the exchange-correlation energy. (In atomic units where $e^2=\hbar=m=1$, the unit of distance is 1 bohr=0.529 Å, and the unit of energy is 1 hartree=27.21 eV.)

r_s (bohrs)	$a(r_s)$ (bohrs)	W (eV)	$W+\dfrac{e^2}{2(r_s+a)}$ (eV)	I (eV)
2	1.58	3.78	7.58	7.99
3	1.34	3.36	6.49	6.45
4	1.23	2.90	5.50	5.42
5	1.16	2.54	4.75	4.68
6	1.11	2.25	4.16	4.12

which is clearly proportional to $(R+a)^{-2}$. The local-density approximation gives accurate ionization energies even for particles as small as a single atom. The self-interaction[26] error of this approximation is not a serious one when the ionization energy is computed as a difference of total energies, as it is here.

The energy of a metallic particle of radius R, charged with Z excess electrons, is thus

$$E_Z=E_0-ZW+\frac{Z^2e^2}{2(R+a)} . \tag{14}$$

The electron affinity (binding energy of one excess electron) is

$$A=E_0-E_1=W-\frac{e^2}{2(R+a)} , \tag{15}$$

and the ionization energy (binding energy of the least-bound electron in the neutral particle) is

$$I=E_{-1}-E_0=W+\frac{e^2}{2(R+a)} . \tag{16}$$

Equations (15) and (16) may be expressed in another way: The Mulliken electronegativity[27] is

$$\tfrac{1}{2}(I+A)=W , \tag{17}$$

and the chemical hardness[28] is

$$\tfrac{1}{2}(I-A)=\frac{e^2}{2(R+a)} , \tag{18}$$

the inverse of the capacitance $R+a$.

As a first numerical test of these new results, Eq. (16) for I as a function of R may be plotted in Fig. 1 of Ref. 9, which shows the results of Ekardt's calculations[9] for ionization energies of jellium spheres with $r_s=4$ and $3 \leq N^* \leq 168$. Apart from shell-structure oscillations in I versus R, the agreement is good. In particular, Eq. (16) accurately describes the ionization energies for small particles with half-filled valence shells.

The parameter a, which is of great importance for very small particles, has been omitted in previous theories[2,6,15–18] of the charging energy. Except for the early work of Kubo[2] and that of Cini,[6] these previous theories[15–18] have been based nonrigorously upon a comparison between the classical image potential experienced by a test charge outside a metallic sphere and outside a semi-infinite metal with a planar surface. This approach leads to Eqs. (1) and (2), with coefficients $+\frac{3}{8}$ and $-\frac{5}{8}$. The coefficients $+\frac{1}{2}$ and $-\frac{1}{2}$ were asserted in Ref. 18, but were obtained there via an incorrect evaluation of a required limit. Note that the classical image-potential formulas are valid only far outside the surface, and are essentially irrelevant to the determination of the work function. In fact the local-density approximation for $E_{\mathrm{xc}}[n]$, which asymptotically yields *no* image potential, still accurately predicts the work functions[29] of bulk metals and the ionization energies[25] of atoms.

B. Atoms as spherical metallic particles

As a second and more extreme numerical test, Table I applies Eq. (16) to the smallest jellium spheres with half-filled valence shells—those with $N^*=1$ electron, and radius $R=r_s$. The bulk work functions W were computed self-consistently by the method of Ref. 29 within the local-density approximation for $E_{\mathrm{xc}}[n]$, using the Ceperley-Alder correlation[30] as parametrized in Ref. 31. The ionization energies I were computed with no approximation. Evidently, Eq. (16) extrapolates successfully to the very smallest particles, although the physics behind its derivation is only qualitatively (not quantitatively) correct in this limit.

As a final numerical test, Table II applies Eqs. (15) and (16) to the smallest real microparticles with half-filled valence shells—the monovalent atoms ($R=r_s$). Remarkably, the atomic ionization energies[32] and electron affinities[33] are predicted reasonably well. Reversing the viewpoint, one may then use known atomic values of I and A to predict the work function[34] via Eq. (17), which was first present as a semiempirical relationship by Chen,

TABLE II. Test of Eqs. (15) and (16) for monovalent atoms. I and A are the measured ionization energy and electron affinity of the atom. W is the measured bulk polycrystalline work function, and r_s the measured bulk density parameter. See also the caption of Table I.

Element	W^{a} (eV)	$r_s{}^{\mathrm{b}}$ (bohrs)	$a(r_s)$ (bohrs)	$W+\frac{e^2}{2(r_s+a)}$ (eV)	I^{c} (eV)	$W-\frac{e^2}{2(r_s+a)}$ (eV)	A^{d} (eV)
Li	2.9	3.25	1.31	5.9	5.39	−0.1	0.62
Na	2.75	3.93	1.24	5.38	5.14	0.12	0.55
K	2.30	4.86	1.17	4.56	4.34	0.04	0.50
Rb	2.16	5.20	1.15	4.30	4.18	0.02	0.49
Cs	2.14	5.63	1.13	4.15	3.89	0.13	0.47
Cu	4.65	2.67	1.40	7.99	7.73	1.31	1.23
Ag	4.26	3.02	1.34	7.38	7.58	1.14	1.30
Au	5.1	3.01	1.34	8.2	9.23	2.0	2.31

[a] Reference 34.
[b] Reference 36.
[c] Reference 32.
[d] Reference 33.

Wentworth, and Ayala.[35] The bulk density parameter[36] r_s may be estimated by solving Eq. (18) in the form

$$r_s + a(r_s) = e^2/(I - A) \ . \tag{19}$$

The utility of this formula is more conceptual than computational. For the hydrogen atom, where the right-hand side equals 2.12 bohrs, Eq. (19) has no solution in the range where $a(r_s)$ is known, reflecting the absence of a zero-pressure metallic phase.

C. Equilibrium charge and stability of a cluster

The equilibrium charge on a metallic microparticle in contact with an electron bath of chemical potential μ and a heat bath of temperature T may be found by using Eq. (14) in the grand-canonical ensemble, following van Staveren *et al.*[17] The present discussion is restricted to $T=0$. The particle will be strictly neutral if $-I < \mu < -A$, i.e., if

$$|W + \mu| < \frac{e^2}{2(R+a)} \ . \tag{20}$$

This condition may always be achieved by taking μ sufficiently close to $-W$.

Finally, consider the binding energy of the least-bound electron in a particle which carries $Z > 0$ excess electrons:

$$E_{Z-1} - E_Z = W - (Z - \tfrac{1}{2}) \frac{e^2}{(R+a)} \ . \tag{21}$$

The particle is stable against field emission of an electron if this expression is positive, i.e., if

$$Z < W \frac{R+a}{e^2} + \tfrac{1}{2} \ . \tag{22}$$

When the excess electron number Z is chosen to minimize the energy E_Z, Z increases with R, but of course the surface charge density $Ze/4\pi R^2$ vanishes as $R \to \infty$. The inequality (22) may be recast:

$$N^* > \left[\frac{(Z - \frac{1}{2})e^2}{W r_s} - \frac{a}{r_s} \right]^3 \ . \tag{23}$$

As Ishii[22] has observed, the smallest number of atoms that can bind Z excess electrons increases very rapidly with Z (Table III).

TABLE III. The smallest number of monovalent atoms that can bind Z excess electrons, from Eq. (23). r_s is the bulk density parameter. The metal particle is treated as a jellium sphere.

Z	$r_s = 2$	$r_s = 4$	$r_s = 6$
1	2	1	1
2	98	34	23
3	553	172	115
4	1647	494	325

TABLE IV. Test of Eq. (26) for neutral jellium spheres with electron number $N^* = 1$ and radius $R = r_s$. ε_{coh} is the exact cohesive energy from Eq. (27). ε is the mean total energy per electron in an infinite jellium, and σ is the surface energy within the local-density approximation. (1 eV/bohr^2 = 57 219 ergs/cm^2.)

r_s (bohrs)	ε (eV)	$\sigma 4\pi r_s^2$ (eV)	ε_{coh} (eV)
2	0.06	−0.76	0.11
3	−1.82	0.44	0.81
4	−2.10	0.57	0.76
5	−2.06	0.53	0.65
6	−1.93	0.47	0.53

III. COHESIVE ENERGY AND SURFACE TENSION

The link between microcosm and macrocosm is also reflected in energy differences which involve no charging. For example, the mean total energy per electron in a neutral jellium sphere of radius R is

$$\varepsilon + \frac{\sigma 4\pi R^2}{N^*} = \varepsilon + \sigma 4\pi r_s^2 \frac{r_s}{R} \ , \tag{24}$$

where

$$\varepsilon = \frac{1.1050\hbar^2}{m r_s^2} - \frac{0.4582 e^2}{r_s} + \varepsilon_c \tag{25}$$

is the mean total energy per electron in infinite jellium, and σ is the surface energy. Table IV shows ε and σ as functions of r_s, for the Ceperley-Alder correlation energy $\varepsilon_c(r_s)$.[30,31] The surface energy σ was calculated self-consistently within the local-density approximation, following the method of Ref. 29. The right-hand side of Eq. (24) may be plotted on Fig. 2 of Ref. 9, which shows the results of Ekardt's calculation[9] for the mean energy per electron of jellium spheres with $r_s = 4$ and $3 \le N^* \le 168$. Apart from shell-structure oscillations, the agreement is good.

In the extreme limit of a single monovalent atom ($N^* = 1$), Eq. (24) predicts that the cohesive energy (energy per atom needed to break up the solid into neutral

TABLE V. Test of Eq. (26) for monovalent elements. ε_{coh} is the measured cohesive energy from Ref. 36, and σ is the measured surface energy extrapolated to temperature absolute zero in Ref. 37.

Element	$\sigma 4\pi r_s^2$ (eV)	ε_{coh} (eV)
Li	1.21	1.63
Na	0.89	1.11
K	0.75	0.93
Rb	0.69	0.85
Cs	0.66	0.80
Cu	2.80	3.49
Ag	2.50	2.95
Au	3.00	3.81

atoms) is just the work done to create the surface of the atom:

$$\varepsilon_{\mathrm{coh}} \approx \sigma 4\pi r_s^2 \ . \tag{26}$$

A similar relationship with a different numerical coefficient was presented by Tyson and Miller,[37] and discussed by Rose, Smith, and Ferrante.[38] Table IV compares the approximation of Eq. (26) to the exact cohesive energy of jellium,

$$\varepsilon_{\mathrm{coh}} = \left(\frac{3e^2}{5r_s} - I \right) - \varepsilon \ . \tag{27}$$

The term in parentheses in Eq. (27) is the total energy of a neutral jellium sphere containing one electron; I is the exact ionization energy from Table I. Except for $r_s = 2$, where jellium is far out of equilibrium, Eq. (26) works reasonably well. In the high-density ($r_s \to 0$) limit, $\varepsilon_{\mathrm{coh}}$ and σ both tend towards $-\infty$. In the metallic range ($2 \le r_s \le 6$), the correlation energy ε_c is needed to make jellium cohere ($\varepsilon_{\mathrm{coh}} > 0$).

Equation (26) also applies to real metals (Table V). The estimate would be improved by using, instead of the area $4\pi r_s^2$ of the Wigner-Seitz sphere, the area of the Wigner-Seitz polyhedron, which is 10% bigger for the body-centered cubic lattice. Once again, a monovalent atom may be regarded as a small metallic particle.

Finally, note that Eq. (26) applies even to nuclear matter:[39] From the semiempirical formula for nuclear binding energy,[40] the left-hand side equals 15.6 MeV while the right-hand side equals 17.2 MeV. A single nucleon (neutron or proton) may be regarded as a small sphere of nuclear matter.

Note added in proof. The parameter "a" of Eq. (14) and following equations is not strictly equal to the distance from the Gibbs surface to the centroid of excess charge. A better estimate may be $a \cong 1.54$ bohrs, independent of r_s. In a subsequent article, "a" will be defined and evaluated. Numerical tests of Eqs. (15) and (16) will be presented for multi-atom clusters as well as single atoms.

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[1] W. P. Halperin, Rev. Mod. Phys. **58**, 533 (1986); A. W. Castleman, Jr. and R. G. Keesee, Acc. Chem. Res. **19**, 413 (1986).

[2] R. Kubo, J. Phys. Soc. Jpn. **17**, 975 (1962).

[3] W. D. Knight, K. Clemenger, W. A. de Heer, W. A. Saunders, M. Y. Chou, and M. L. Cohen, Phys. Rev. Lett. **52**, 2141 (1984).

[4] N. W. Ashcroft and D. C. Langreth, Phys. Rev. **155**, 682 (1967).

[5] N. D. Lang and W. Kohn, Phys. Rev. B **1**, 4555 (1970); **3**, 1215 (1971).

[6] M. Cini, J. Catalysis **37**, 187 (1975).

[7] J. L. Martins, R. Car, and J. Buttet, Surf. Sci. **106**, 265 (1981).

[8] D. E. Beck, Solid State Commun. **49**, 381 (1984).

[9] W. Ekardt, Phys. Rev. B **29**, 1558 (1984).

[10] M. Y. Chou, A. Cleland, and M. L. Cohen, Solid State Commun. **52**, 645 (1984).

[11] M. Manninen, Phys. Rev. B **34**, 6886 (1986).

[12] Y. Ishii, S. Ohnishi, and S. Sugano, Phys. Rev. B **33**, 5271 (1986).

[13] W. D. Knight, W. A. de Heer, W. A. Saunders, K. Clemenger, M. Y. Chou, and M. L. Cohen, Chem. Phys. Lett. **134**, 1 (1987).

[14] J. L. Martins, J. Buttet, and R. Car, Phys. Rev. B **31**, 1804 (1985).

[15] J. M. Smith, Am. Inst. Aeronaut. Astronaut. J. **3**, 648 (1965).

[16] D. M. Wood, Phys. Rev. Lett. **46**, 749 (1981).

[17] M. P. J. van Staveren, H. B. Brom, L. J. de Jongh, and Y. Ishii, Phys. Rev. B **35**, 7749 (1987).

[18] A. Herrmann, E. Schumacher, and L. Wöste, J. Chem. Phys. **68**, 2327 (1978).

[19] N. D. Lang and W. Kohn, Phys. Rev. B **7**, 3541 (1973). See also P. A. Serena, J. M. Soler, and N. Garcia, *ibid.* **34**, 6767 (1986).

[20] D. E. Beck, Phys. Rev. B **30**, 6935 (1984).

[21] D. R. Snider and R. S. Sorbello, Phys. Rev. B **28**, 5702 (1983).

[22] Y. Ishii, Solid State Commun. **61**, 227 (1987).

[23] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).

[24] J. P. Perdew, R. G. Parr, M. Levy, and J. L. Balduz, Jr., Phys. Rev. Lett. **49**, 1691 (1982).

[25] O. Gunnarsson and B. I. Lundqvist, Phys. Rev. B **13**, 4274 (1976).

[26] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[27] R. S. Mulliken, J. Chem. Phys. **2**, 782 (1934).

[28] R. G. Parr and R. G. Pearson, J. Am. Chem. Soc. **105**, 7512 (1983).

[29] R. Monnier and J. P. Perdew, Phys. Rev. B **17**, 2595 (1978); R. Monnier, J. P. Perdew, D. C. Langreth, and J. W. Wilkins, *ibid.* **18**, 656 (1978).

[30] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).

[31] S. H. Vosko, L. Wilk, and M. Nusair, Can. J. Phys. **58**, 1200 (1980).

[32] C. E. Moore, *Ionization Potentials and Ionization Limits Derived from the Analyses of Optical Spectra,* Natl. Bur. Stand. (U.S.), Nat. Stand. Ref. Data Ser. No. 34 (U.S. GPO, Washington, D.C., 1970), p. 1.

[33] H. Hotop and W. C. Lineberger, J. Phys. Chem. Ref. Data **14**, 731 (1985).

[34] H. B. Michaelson, J. Appl. Phys. **48**, 4729 (1977).

[35] E. C. M. Chen, W. E. Wentworth, and J. A. Ayala, J. Chem. Phys. **67**, 2642 (1977).

[36] C. Kittel, *Introduction to Solid State Physics,* 6th ed. (Wiley,

New York, 1986).

[37] W. R. Tyson and W. A. Miller, Surf. Sci. **62**, 267 (1977).

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

[39] J. H. Rose, J. P. Vary, and J. R. Smith, Phys. Rev. Lett. **53**, 344 (1984).

[40] H. A. Bethe and P. Morrison, *Elementary Nuclear Theory,* 2nd ed. (Wiley, New York, 1966).