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Positron work function and deformation potential

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Electron and positron chemical potentials at a given crystal volume are obtained from first-principles density-functional calculations. The calculated chemical potentials are used to obtain the positron work function and deformation potential. The results are compared with previous calculations for several simple metals, and with experimental measurements of aluminum and copper.

INTRODUCTION AND THEORY

The positron work function is of interest in the study of the behavior of positrons at metal surfaces,[1] and the positron deformation potential is related to positron diffusion in metals.[2] The experimental measurements of these quantities can also be used as a test of theoretical calculations of the electron and positron chemical potentials and the surface dipole potential of metals.

The work function ϕ_- of a metal can be expressed as[3]

$$\phi_- = D - \mu_- , \tag{1}$$

where D is the surface dipole potential barrier against electron escape, and μ_- is the internal electron chemical potential. The positron will experience just the negative of this potential barrier upon emission from the surface, so its work function is given by

$$\phi_+ = -D - \mu_+ , \tag{2}$$

with μ_+ the positron chemical potential. The emission of a positronium atom from the surface can also be described by a work function,

$$\phi_{Ps} = \phi_+ + \phi_- - 0.5 \text{ Ry} , \tag{3}$$

which is less than the positron work function because the electron work function is usually less than 0.5 Ry. The internal electron chemical potential μ_- and the positron chemical potential μ_+ are purely bulk properties that can be obtained from a band structure calculation. The quantity μ_- is equal to the Fermi energy and μ_+ is the lowest energy of the positron energy band. These quantities are measured relative to the "crystal zero" of the electrostatic potential, which for the spherical cellular model to be described below, occurs at the cell boundary.

The deformation potential model is used in the treatment of the contribution to the relaxation time by positron-acoustical phonon scattering, which is a quantity that is needed to calculate the positron diffusion constant.[2] The deformation potential E_d is defined as $\Omega \partial E / \partial \Omega$ where $E(\Omega)$ is the energy of the lowest positron Bloch state at the crystal volume Ω, provided we take the local variation of the electron density into account. Bergersen *et al.*[2] express E_d as the sum of three contributions. The first two come from the zero-point energy E_0 and the electron-positron correlation energy E_{corr}. In terms of these quantities, the positron chemical potential is given by $\mu_+ = E_0 + E_{\text{corr}}$. The third contribution to the deformation potential comes from a charge transfer between regions of different density. This generates an electrostatic potential equivalent to a surface dipole term that compensates the shift in μ_- due to crystal dilation, therefore maintaining a constant electron chemical potential throughout the crystal. Consequently, we can calculate the deformation potential from

$$E_d = \Omega \frac{d}{d\Omega} (\mu_+ + \mu_-) . \tag{4}$$

The deformation potential and the positronium work function depend on $\mu_+ + \mu_-$, and therefore do not involve the surface dipole potential D, which, being a surface property, is more difficult to calculate accurately. Lang and Kohn[4] used the jellium model values of D and μ_- to calculate ϕ_- according to Eq. (1). Their work functions were in good agreement with experiment even for the higher density metals for which the jellium values of the chemical potential μ_- are too large. This was shown by Heine and Hodges[5] to be due to a negative feedback mechanism in which the outward penetration of the electrons which determines the dipole potential D is inversely related to the magnitude of μ_-. As a result, the variation in the work function is much smaller than that in μ_- and D. In this work, we circumvent calculating D by using our calculated values of μ_- and measured work functions[6] to obtain D from Eq. (1).

CALCULATIONS AND RESULTS

We calculate the chemical potential and the electronic density of the metal from first principles using the self-consistent density functional method and the local density approximation, with the Hedin-Lundqvist[7] form of the exchange-correlation energy. Since full details of our method are being published elsewhere we only give a brief description here. To calculate the band structure, we solve the effective one-electron Schrödinger equation by applying the set of boundary conditions for the Bloch wave functions over the surface of a Wigner-Seitz sphere.[8] When used to calculate the band structure and the bulk properties of simple metals,[9] the results of the spherical cellular method were in good agreement with the calculations of Moruzzi, Janak, and Williams[10] (MJW), who performed a self-consistent Korringa-Kohn-Rostoker (KKR) calculation with muffin-tin densities in a polyhedral cell. In particular, our chemical potentials were in good agreement with results based on the MJW calculations.[11] The MJW calculations are tabulated only for the equilibrium lattice constant, however, while for the present problem the volume dependence of μ_- is required. By using the spherical cellular method we could calculate such quantities as the chemical potential and the electron density at any volume.

We apply the spherical-cell approximation again in the calculation of the positron chemical potential μ_+, and treat the electron-positron correlation in a local density approximation by including it in the effective potential of the positron. The effective potential a positron would see has the form, in atomic units,

$$V(r)=\frac{2Z}{r}-2\int\frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'+\epsilon^{e-p}(r)\,, \tag{5}$$

where Z is the atomic number, $\rho(r)$ is the total electron density, and $\epsilon^{e-p}(r)$ is the electron-positron correlation energy. For this quantity we use a recently published parametrized form for the energy of a single positron in a uniform electron gas by Boroński and Nieminen.[12] In previous calculations of the positron chemical potential,[1,3] the Schrödinger equation was solved with only the electrostatic potential, i.e., the first two terms of Eq. (5), thus obtaining the "zero-point energy" E_0. The correlation energy of the positron was calculated at the average valence electron density of the metal in the jellium model, and was then added to E_0 to obtain μ_+. As we describe below, we find that our complete local-density approximation (LDA) results for μ_+ are in quite good agreement with these earlier calculations. We also compared the LDA result with a calculation in which the correlation energy is treated as a first-order perturbation to the electrostatic potential, and found the effect on μ_+ to be less than 0.01 eV. The insensitivity of μ_+ to the use of a self-consistent $\epsilon^{e-p}(r)$ can be explained on the basis that the positron wave function is largest in the interstitial region where the electron density is nearly constant, and that $\epsilon^{e-p}(r)$ is a weakly varying function of electron density.[12]

For thermalized positrons, around room temperature, ≈ 0.025 eV, μ_+ is nearly the energy of the bottom of their energy band. The band effective mass, also of interest in positron calculations, can be obtained from the curvature of the energy band at $\mathbf{k}=0$. For instance, for aluminum we found a positron band effective mass of $1.05m$, which is in agreement with other calculations.[13]

In Table I we present the components of the positron work function. The surface dipole potential D was obtained from the experimental ϕ_- and the calculated μ_-. Also given are the experimental values of ϕ_+ of Al and Cu.[14] The experimental work functions in this table are averages over different faces.

Gullikson and Mills have measured the face-dependent positron work function for Al(100) and Al(111) from 20 to 300 K.[15] To calculate the face dependence of ϕ_+ we note that the chemical potential is a bulk property, so the face dependence is due solely to the surface dipole potential. We can again obtain this quantity from the measured electron work function for the various faces, 4.41 eV for Al(100) and 4.24 eV for Al(111).[16] Assuming that the temperature dependence of

TABLE I. Components of the positron work function ϕ_+ for simple metals. Energies are in eV.

Metal	r_s	μ_+	μ_-	ϕ_-(expt)[a]	D	ϕ_+	ϕ_+(expt)
Li	3.26	−5.27	−2.53	2.90	0.37	4.90	
Na	3.93	−5.28	−2.41	2.75	0.34	4.94	
K	4.86	−5.32	−2.31	2.30	0.0	5.32	
Mg	2.65	−4.59	−2.04	3.66	1.62	2.97	
Al	2.07	−4.00	−0.43	4.28	3.85	0.15	−0.07[b]
Cu	2.67	−3.51	−1.06	4.65	3.59	−0.08	−0.4[c]

[a] Reference 6.

[b] Reference 19.

[c] Reference 13.

TABLE II. Positron work function of Al(100) and Al(111) at $T=20$ and 300 K. The chemical potentials are in eV, positron work function is in meV.

T	r_s	μ_-	μ_+		ϕ_+	$\phi_+(\text{expt})^{\text{a}}$
20	2.061	-0.325	-3.987	(100)	-98	-300
				(111)	72	-80
300	2.07	-0.432	-0.4005	(100)	27	-155
				(111)	197	65

[a]Reference 15.

the chemical potentials is due to the lattice thermal expansion, we can use the thermal expansion data to convert the volume dependence of these quantities to temperature dependence. Due to the negative feedback mentioned earlier, we expect the temperature dependence of the electron work function to be negligible. This is also confirmed by experiment where it is found to be much smaller than the temperature variation of the positron work function.[15] In Table II we present the results of calculated ϕ_+ for Al(100) and Al(111) at 20 and 300 K along with the experimental measurements. The observed change in ϕ_+ with temperature is 145 meV, independent of face. This provides strong evidence that the temperature dependence of ϕ_+ is indeed due essentially to changes in $\mu_+ + \mu_-$ with volume. Our calculated change in ϕ_+ is 125 meV, in quite good agreement with the experiment.

We obtained the deformation potential by calculating μ_+ and μ_- as functions of r_s near the equilibrium r_s of the metal, and then using

$$E_d = \frac{r_s}{3}\frac{d}{dr_s}(\mu_+ + \mu_-) \; .$$

The results are given in Table III along with calculated values of E_d by Bergersen *et al.*, and experimental results for Al and Cu. To obtain the experimental value for copper, we used the slope $(d/dT)(\phi_+ + \phi_-) = 5\times 10^{-4}$ eV/K given by Schultz and Lynn,[17] and the $T=200$ K value of the thermal expansion coefficient, $\alpha = 15.2\times 10^{-6}\ \text{K}^{-1}$, in $d/dT(\phi_+ + \phi_-) = -3\alpha E_d$.[18] This, however, involves some uncertainty because the data of Schultz and Lynn extended from 40 to 300 K, and the thermal expansion coefficient is temperature dependent. For this reason, the extremely close agreement of calculation with experiment may be somewhat fortuitous.

TABLE III. Deformation potential and its electron and positron components for simple metals. The work of Bergersen *et al.* (Ref. 2) and available experimental values are given for comparison. Energies are in eV.

Metal	$\Omega \frac{d\mu_-}{d\Omega}$	$\Omega \frac{d\mu_+}{d\Omega}$	E_d	$E_d{}^{\text{a}}$	$E_d(\text{expt})$
Li	-1.46	-0.05	-1.51	-2.58	
Na	-1.57	-0.26	-1.73	-2.04	
K	-1.37	-0.32	-1.69	-1.77	
Mg	-3.11	-0.66	-3.77	-5.17	
Al	-8.24	-1.39	-9.63	-8.57	-11.7^{b}
Cu	-7.76	-2.66	-10.42		-10.9^{c}

[a]Reference 2.
[b]Reference 15.
[c]Reference 17.

CONCLUSION

In the calculation of the positron chemical potential, there is not a significant numerical difference between previous calculations, treating correlation in the jellium model, and this work, treating correlation in the local-density approximation. Our assumption that the temperature dependence of μ_+ was due to the lattice thermal expansion, and not any intrinsic effects, seems to be justified by the very good agreement of the calculated temperature dependence of the positron work function with experiment. The experimental value of the deformation potential is obtained from the data based on the same assumption and here, too, the agreement between theory and experiment is good. Finally, we emphasize that the strong volume dependence of the electron chemical potential indicates that this quantity has to be calculated at the correct experimental value of r_s in these calculations.

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