

Dependence of the vacancy formation energy on the electronic density parameter for noble metals and metallic hydrogen

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ABSTRACT. We calculated the variation of the vacancy formation energy with the electron density parameter, r_s , using density functional formalism within the approach given by Fumi. We took five decreasing values of r_s , which are 1, 2, 3, 4 and 5% less than the value of r_s at atmospheric pressure for noble metals and less than the expected equilibrium value for metallic hydrogen. For every case, we found that the vacancy formation energy increases when r_s decreases.

RESUMEN. Calculamos la variación de la energía de formación de vacancias con respecto del parámetro de densidad electrónica, r_s , por medio del formalismo de funcional de densidad, dentro del enfoque dado por Fumi. Tomamos cinco valores distintos de r_s , que son 1, 2, 3, 4 y 5% menores que los correspondientes valores de r_s a presión atmosférica, para los metales nobles y menores que el valor esperado en equilibrio para r_s en el caso de hidrógeno metálico. Encontramos para todos los casos que cuando r_s decrece, la energía de formación de vacancias crece.

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1. INTRODUCTION

It is well known that vacancies may have influence on the mechanical, optical or electrical properties of materials. In this work we are interested on the variation, for noble metals and metallic hydrogen, of the vacancy formation energy with the electronic density parameter, r_s , defined by $(4/3)\pi r_s^3 = (1/n_0)$, where n_0 is the average electronic density in the material. Variations on the density of the material may occur because of changes in pressure or temperature of the sample and these lead to changes in the parameter r_s .

The vacancy energy, E^f , can be written as [2,4]

$$E^f = \Delta T + \Delta E_{xc} + \Delta E_c + \Delta E_r,$$

where ΔT is the change in kinetic energy of the electrons, ΔE_{xc} is the change in exchange and correlation energy, ΔE_c is the change in electrostatic energy and ΔE_r is the change in energy because of lattice relaxation. All these changes happen when the vacancy is formed. The calculation of E^f turns out to be quite complex and computer time consuming [1-7], even for zero temperature. As a first approximation E^f can be written as [1]

$$E^f = \Delta E_{\text{eigen}} - (2/5)E_F, \quad (1)$$

where ΔE_{eigen} is the change in the energy eigenvalues of the electrons and E_F is the Fermi energy of the metal. The expression for ΔE_{eigen} is (see for example Refs. [1,8])

$$\Delta E_{\text{eigen}} = -\frac{2}{\pi} \sum_{\ell=0} (2\ell + 1) \int_0^{k_F} dk k \eta_{\ell}(k), \quad (2)$$

where k_F is the Fermi wave vector, $\eta_{\ell}(k)$ is the corresponding phase shift of wave vector k and angular momentum ℓ produced by scattering from the vacancy.

From Eqs. (1) and (2), and using some other approximations, Fumi [1] gives for E^f :

$$E^f = \frac{1}{6} E_F, \quad (3)$$

where E_F is the Fermi energy of the material.

To obtain E^f and its dependence on r_s we use density functional theory to calculate ΔE_{eigen} with Eq. (2) and then we use Eq. (1) to find the vacancy formation energy. This approach has been used successfully to predict the vacancy formation energy of noble metals and it has been extended to predict the vacancy formation energy for metallic hydrogen (9). This procedure was carried out for every one of the five values of r_s for each metal.

Section 2 is used to describe, briefly, the equations from density functional formalism [10,11], which we solved to calculate self-consistently the phase shifts necessary for Eq. (3). Section 3 is for results and discussion.

2. ELECTRONIC DENSITIES AROUND VACANCIES

We use the density functional formalism of Hohenberg, Kohn and Sham [10,11] to obtain the electronic densities and the corresponding phase shifts (which are necessary to calculate ΔE_{eigen}). Because we have used this formalism in previous works for the calculation of properties of metals from first principles (see for example Refs. [12 to 17]), where we give numerical details of the solution of the corresponding equations, we will omit those details here and we only give a brief description of the formalism.

The central result of the density functional theory states that there exists a one-body local potential, $V_{\text{eff}}(r)$, which through the one-body Schrödinger equation,

$$\left[-\frac{1}{2}\nabla^2 + V_{\text{eff}}(r)\right]\varphi_i(r) = \epsilon_i\varphi_i(r),$$

generates the set of wave functions $\varphi_i(r_i)$ and the exact ground state density of the system through the independent particle density expression:

$$n(r) = \sum_{\epsilon_i < \epsilon_f} [\varphi_i(r)(r)]^2,$$

where the sum extends up to the Fermi energy.

The effective potential is

$$V_{\text{eff}}(r) = -\Phi(r) + \frac{\delta E_{\text{xc}}[n(r)]}{\delta n(r)},$$

where $\Phi(r)$ is the total electrostatic potential of the system, and $E_{\text{xc}}[n(r)]$ is the exchange-correlation energy of the system.

When we omit gradient corrections it is possible to obtain

$$\frac{\delta E_{\text{xc}}[n(r)]}{\delta n(r)} = \frac{d}{dn}[n(r)\epsilon_{\text{xc}}(r)], \quad (4)$$

where $\epsilon_{\text{xc}}[n(r)]$ is the exchange-correlation energy per particle in a homogeneous electron gas of density $n(r)$.

For the exchange-correlation contribution to the effective potential, Eq. (4), we use the expression given by Gunnarson and Lundquist [18] in double Rydbergs:

$$\begin{aligned} V_{\text{xc}}(r) &= \frac{\delta E_{\text{xc}}[n(r)]}{\delta n(r)} \\ &= -0.619 \left[\frac{1}{r_s} + 0.0585 \ln \left(1 + \frac{11.4}{r_s} \right) \right], \end{aligned} \quad (5)$$

where

$$\frac{4}{3}\pi r^3 = \frac{1}{n(r)}.$$

In order to have $V_{\text{eff}}(r)$ vanishing at large r , the exchange-correlation part is rescaled to

$$V_{\text{xc}}(r) \rightarrow V_{\text{xc}}[n(r)] - V_{\text{xc}}[n_0], \quad (6)$$

where n_0 is the equilibrium density.

The electrostatic potential obeys Poisson's equation:

$$\nabla^2 \Phi = -4\pi D(r), \quad (7)$$

where $D(r)$ is the total charge density.

For this case, $D(r)$ corresponds to a vacancy in jellium, *i.e.*,

$$D(r) = n_0\theta(r_s - R_{\text{WS}}) - n(r), \quad (8)$$

where $\theta(x)$ is the step function and R_{WS} is the Wigner-Seitz radius.

The phase shifts used in the calculation of ΔE_{eigen} are a subproduct from the self-consistent calculation of the electron densities. They are produced by the scattering of the electrons by $V_{\text{eff}}(r)$.

TABLE I. Phase shifts at the Fermi level $\eta_\ell(K_F)$ from the self-consistent calculations at atmospheric pressure. The values of r_s correspond to values for which the measurements were taken, except for hydrogen for which we took the predicted equilibrium value [12].

		Phase Shifts							
		η_0	η_1	η_2	η_3	η_4	η_5	η_6	η_7
H									
$r_s = 1.0$		-0.3649	-0.1764	-0.0690	-0.0254	-0.0093	-0.0035	-0.0013	-0.0005
Cu									
$r_s = 2.67$		-0.6135	-0.2181	-0.0493	-0.0043	-0.0008	-0.0000		
Ag									
$r_s = 3.01$		-0.6497	-0.2209	-0.0445	-0.0047	-0.0001	-0.0000		
Au									
$r_s = 3.02$		-0.6508	-0.2210	-0.0444	-0.0046	-0.0001	-0.0000		

TABLE II. Calculated changes of ΔE_{eigen} , in electron volts, with r_s for each metal. The values of ΔE_{eigen} correspond to values of r_s which are 0, 1, 2, 3, 4, and 5% smaller than the corresponding value of r_s at atmospheric pressure for noble metals and smaller than the expected equilibrium value for metallic hydrogen [12].

	Cu	Ag	Au	H
$\Delta E_{\text{eigen} 0}$	4.1939	3.2413	3.2201	31.767
$\Delta E_{\text{eigen} 1}$	4.2873	3.3069	3.2850	32.607
$\Delta E_{\text{eigen} 2}$	4.3828	3.3759	3.3530	33.306
$\Delta E_{\text{eigen} 3}$	4.4802	3.4483	3.4246	34.024
$\Delta E_{\text{eigen} 4}$	4.5794	3.5245	3.4998	35.760
$\Delta E_{\text{eigen} 5}$	4.6805	3.6045	3.5788	35.515

3. RESULTS AND DISCUSSION

In order to obtain the required phase shifts to obtain E^f , we calculated the electronic density around a vacancy solving the set of self-consistent equations given in Sect. 2 five different times for each material. This was because we took a set of five different values of r_s for each material, which were 1, 2, 3, 4 and 5% less than the initial values corresponding to those for which we have experimental results of E^f . In the case of metallic hydrogen we took $r_s = 1.0$ (a.u), which is the expected equilibrium value [12], as the initial value.

In Table I we exhibit the resulting phase shifts produced by the scattering of the electrons by $V_{\text{eff}}(r)$, which came out from the self-consistent calculation of the electronic densities, are given in Table I at the Fermi level, K_F , and at atmospheric pressure. We obtained $\eta_\ell(k)$ for values of k corresponding to a 24 point Gaussian integration to calculate ΔE_{eigen} from Eq. (2). The values for ΔE_{eigen} for each material are shown in Table II in electron-volts, for every one of the five values of r_s . In Table III we show the calculated values of E^f , with the corresponding values of r_s , for each material. We can see that we have a practically linear behavior of E^f with r_s for each material and that the vacancy

TABLE III. Predictions for the variation of the vacancy formation energy (in electron-volts) with r_s for each metal. Experimental results at atmospheric pressure are from: (a) Ref. [20], (b) Ref. [21]. The values of r_s are given in a.u. (1 a.u. = 0.529 Å). Letter (c) refers to the corresponding prediction made with Fumi's formula, Eq. (3). Letter (d) refers to the results from this work.

$\Delta r_s/r_s$ (%)	Cu	Ag	Au	H
0	(1.29 ± 0.02 ^a)	(1.16 ± 0.02 ^a)	(0.97 ± 0.01 ^a)	—
	(1.17 ± 0.1 ^b)	(1.01 ± 0.1 ^b)	(1.01 ± 0.1 ^b)	—
	1.17 ^c	0.92 ^c	0.91 ^c	8.35 ^c
	1.38 ^d	1.03 ^d	1.02 ^d	11.72 ^d
1	1.20 ^c	0.94 ^c	0.93 ^c	8.52 ^c
	1.42 ^d	1.05 ^d	1.04 ^d	12.15 ^d
2	1.22 ^c	0.96 ^c	0.95 ^c	8.69 ^c
	1.46 ^d	1.07 ^d	1.06 ^d	12.43 ^d
3	1.25 ^c	0.98 ^c	0.97 ^c	8.87 ^c
	1.49 ^d	1.10 ^d	1.09 ^d	12.72 ^d
4	1.27 ^c	1.00 ^c	0.99 ^c	9.06 ^c
	1.53 ^d	1.12 ^d	1.11 ^d	13.01 ^d
5	1.30 ^c	1.02 ^c	0.101 ^c	9.25 ^c
	1.57 ^d	1.15 ^d	1.14 ^d	13.30 ^d

formation energy increases when r_s decreases. This means that it should be more difficult to form a vacancy as the pressure on the sample is increased (the parameter r_s is decreased). The maximum variations in E^f are for the largest change in r_s (−5%) and have the values: for hydrogen 14%, for copper 14%, for silver 12% and for gold 12%. In this table we also show the expected variation from Fumi's prediction, from Eq. (3). We have that the maximum change is 11% for all the considered metals and corresponds also to the largest change in r_s . It should be possible to detect the predicted changes in E^f . It seems that this detection should be easier with the positron trapping technique [20], because it gives a much smaller error on E^f , than with the traditional methods [21]. With the traditional methods the error is about 10% of E^f . Notice that a 5% variation in the parameter r_s corresponds approximately to 15% variation in volume.

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