The Work Function Dependence on the Mean Surface Density of Valence Electrons, and its Relevance to the Field Emission of Electrons

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Abstract: A first-order phenomenological model is described that predicts there is an inverse linear relationship between the work function of a metal ø and the surface density of its valence electrons S, and a positive linear relationship between S and the threshold field E_{BF} for the cold emission of electrons from extended metal surfaces. These findings highlight the apparently paradoxical implication that a high S-value serves to promote the photo emission of electrons, it serves to suppress the field emission of electrons. The model also predicts that the electrochemical potential of a metal is linearly related to its S-value, and provides a surface-related interpretation of the contact potential difference between metals.

1. Introduction

As detailed in the reviews of Lang & Kohn 1971 [1], Halas 2006 [2], Holzl & Schulte 2006 [3], and Mastwijk et al 2007 [4]], the physical origin of the work function of a metal has a long history of theoretical analysis, and the present paper offers a further contribution to this debate. The author's interest in this subject stems from an extended study of the physical processes that control the field emission of electrons from planar metal surfaces [5-8]. The present study was motivated by a seminal investigation by Batrakov's group [9] which, as discussed in a following section, demonstrated that there is an approximately linear relationship between the threshold field for the cold emission of electrons and the work function of the cathode material, and that this in turn is dependent on its crystal structure.

The aim of the present study was to determine if there is a surface parameter of a metal that can be directly related to its work function. The one chosen for investigation in the following analysis was made on the intuitive reasoning that, in the same way that the bulk density of free electrons N determines the bulk properties of a metal, it will be the surface density of valence electrons S that will control its surface properties. As will be shown, the value of S for a given metal depends on the volume density of its free electrons, the valency of the surface atoms, and its crystal structure. The analysis will also show that the S-parameter is related to the electrochemical potential of a metal, and how it determines the value of the contact potential difference between two metals.

2. Electrical Properties of Metals

The bulk electrical properties of metals are fully described by the well-known Drude-Sommerfeld model of electrical conduction which is based on the volume density of free valence electrons N. An important recognition of this model was that only those electrons with

energies near the Fermi energy are free to take part in the conduction process. This consideration was the subject of a recent detailed analysis by Palenskis 2014 [10], in which tabulated data is presented for a range of common metals, that compare the Total Density of free electrons N with the Effective Density N_{EF} of the electrons that are responsible for the experimentally measured parameters. So, for monovalent copper, where $[N_{Cu}]_1$ has a value of $8.47 \times 10^{28} m^{-3}$, the calculated value of N_{EF} is 6.36×10^{26} m^{-3}, giving the ratio of $N_{EF}/N_{Cu} = 0.0075$.

The question however arises as to what happens at the surface of a metal; in particular, why do electrons experience a retaining barrier, or work function, which prevents them from escaping from the surface. This question was reviewed by Mastwijk et al 2007[11], from which it was concluded that the work function barrier results from the interaction between the three competing forces experienced by a valence electron trying to escape from the surface. These are (i) the coulomb attractive force between the electron and the ion cores of the surface atoms, (ii) the repulsive force between the electron and the population of neighbouring surface electrons, and (iii) the attractive quantum mechanical spin coupling force.

From the above observations, it can be intuitively concluded that the variation in work function among different metals is related in some way to the differing distributions of their populations of surface valence electrons. The question therefore arises as to what extent are the electronic surface properties of a metal related to their bulk properties. In particular, is there a relationship between the mean surface density of valence electrons S and a) the bulk volume density of free electrons b) the crystal structure, and c) the effective valency of surface atoms. In this context, it can be reasonably assumed that there will be an abundance of available empty states at the surface, which implies that their freedom will not be restricted as in the bulk.

3. Surface Density of Valence Electrons

As a first approach to obtaining an order-of-magnitude relationship between the N and S values of a metal, consider a meter square conducting cube having a volume density N of free valency electrons, and assume that these are distributed uniformly throughout its volume. However, the important question immediately arises as to what value should be used for the valency of the constituent atoms when calculating values of N. From a physical perspective, all common metals belong to the transition group of elements, which share the same electron configuration with two s-valence electrons in their outermost shell. On the other hand, from a chemical perspective, these same elements frequently exhibit a range of higher valency values as a result of some of the d-shell electrons having lower energies than the outer s-electrons. In fact, it is these "chemical" valency values that are commonly quoted in standard tabulated data. It is therefore an open question as to what value to use for the valency in the "physical" situation of surface of a metal, and consequently, the valency has to be regarded as an uncertain parameter in the following analysis. Finally, as discussed above (Palenskis 2014 [11]), account also has to be taken of the possibility that the "effective" bulk free electron density N_{EF} is significantly lower than the normally quoted values.

3.1 Dependency of ø on S

Returning to the unit sided conducting cube, and assuming that the N bulk valency electrons are uniformly distributed throughout its volume, it follows that the average cell volume δv occupied by each electron will be $1/N$ m^3, so that the cell dimension δl will be $(1/N)^{1/3}$ m , or $N^{-1/3}$ m, with the surface area δA of a cell being $(N^{-1/3})^2$, or $N^{-2/3}$ m^2. Accordingly, the number

of cells, and hence electrons, that intersect the surface of the cube will be $(N^{-2/3})^{-1}$, or in general, the mean surface density of valence S_M according to this model will be

$$S_M = N^{+2/3} \text{ --------------------------------}(1)$$

So, in the case of copper, where from earlier, $[N_{Cu}]_1 = 8.47 \times 10^{28} m^{-3}$, and $[N_{Cu}]_2 = 16.93 \times 10^{28}$, one has

$$[S_{Cu}]_1 = 1.9 \times 10^{19} m^{-2}$$
$$[S_{Cu}]_2 = 3.1 \times 10^{19} m^{-2}$$

Applying this procedure to a range of common metals, one finds

$$[N_{Ag}]_2 = 5.86 \times 10^{28} \rightarrow [S_{Ag}]_2 = 1.8 \times 10^{19} m^{-2}$$

$$[N_{Al}]_3 = 18.1 \times 10^{28} \rightarrow [S_{Al}]_3 = 3.2 \times 10^{19} m^{-2}$$

$$[N_{Ni}]_2 = 18 \times 10^{28} \rightarrow [S_{Ni}]_2 = 3.1 \times 10^{19} m^{-2.}$$

$$[N_{Nb}]_5 = 5.6 \times 10^{28} \rightarrow [S_{Nb}]_5 = 1.5 \times 10^{19} m^{-2}$$

$$[N_{Zn}]_2 = 13.2 \times 10^{28} \rightarrow [S_{Nb}]_2 = 2.6 \times 10^{19} m^{-2.}$$

$$[N_{Pb}]_4 = 13.2 \times 10^{28} \rightarrow [S_{Pb}]_4 = 2.6 \times 10^{19} m^{-2}$$

$$[N_{Ta}]_5 = 27.5 \times 10^{28} \rightarrow [S_{Ta}]_5 = 4.2 \times 10^{19} m^{-2}$$

$$[\qquad N_{Ti}]_4 = 15 \times 10^{28} \rightarrow [S_{Ti}]_4 = 2.8 \times 10^{19} m^{-2}$$

$$[N_{Zr}]_4 = 17 \times 10^{28} \rightarrow [S_{Zr}]_4 = 3.1 \times 10^{19} m^{-2}$$

$$[N_W]_6 = 5.9 \times 10^{28.} \rightarrow [S_W] = 1.55 \times 10^{19} m^{-2}$$

If this set of S-values are now plotted against the corresponding work functions taken from reference to standard tables and other specialist sources [12], one obtains the randomly scattered plot shown below in Figure 1, which clearly shows that there is no consistent correlation between these two parameters. Rather, it would appear that most metals have a tendency to share a common S-value of ~3×10^{19}.

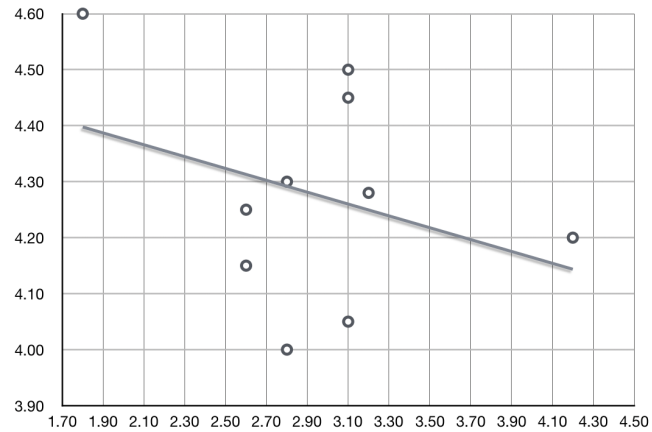| Metal	Surface Density of Valence Electrons S x 10+19	Work Function Ø (eV)
Ag(2)	1.8	4.6
Al(3)	3.2	4.28
Cu(2)	3.1	4.45
Nb(3)	2.8	4.3
Ni(2)	3.1	4.5
Ti(4)	2.8	4.0
Zr(4)	3.1	4.05
Ta(5)	4.2	4.2
Zn(2)	2.6	4.15
Pb(4)	2.6	4.25

Figure 1

3.2 Dependence of S on Crystal Structure

An alternative and more detailed approach to estimating the surface density of free valence electrons S is to take account of the influence of crystal structure and the associated properties of the metal under consideration. For this purpose, reference will be made to Figure 2 which shows the alternative crystal structures of common transition metals.

Common metallic crystal structures

body-centred cubic (bcc)   face-centred cubic (fcc)   hexagonal close-packed (hcp)
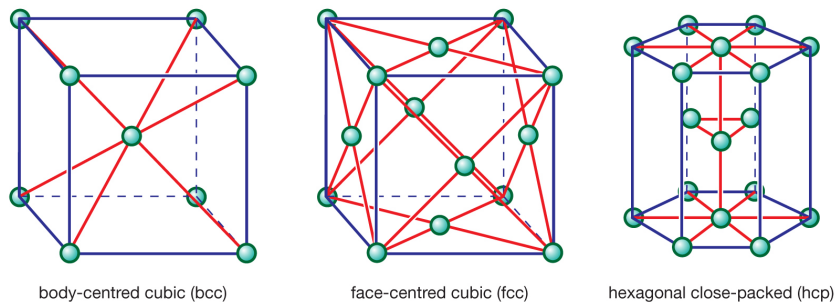
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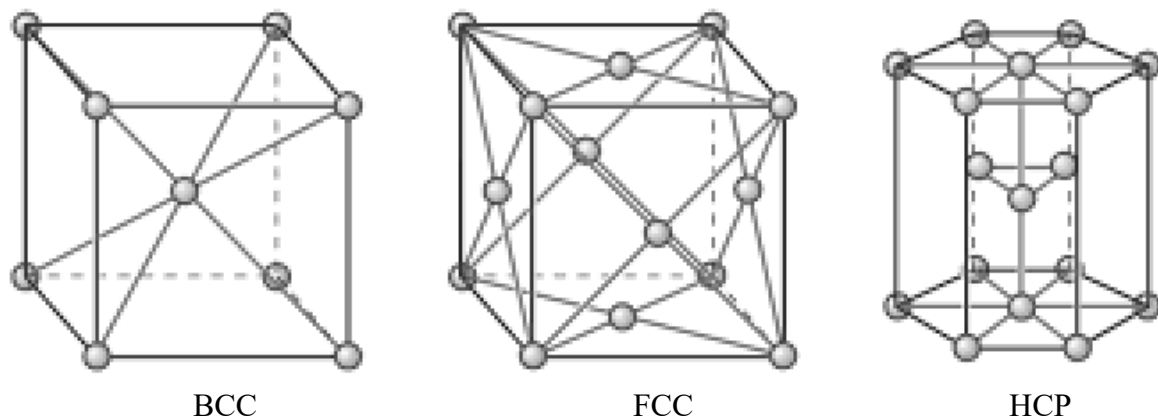
BCC   FCC   HCP

Figure 2

As a first example, consider the case of divalent copper with a FCC cubic structure and a lattice constant of 360pm. It follows that the volume of each unit cell will be $(3.6 \times 10^{-10})^3 = 9.7 \times 10^{29} m^3$, and that the area of each face of its unit cell will be $(3.6 \times 10^{-10})^2 m^2$, or $1.3 \times 10^{-19} m^2$,

so that the number of unit cell faces intersecting unit area of the surface of such a structure will be $1/1.3 \times 10^{19} = 7.6 \times 10^{18}$. To determine how many surface valence electrons are contributed by each unit cell face, assume that each of the valence electrons donated by each of the surface atoms shares its time between the four unit cells immediately below the surface, and the four virtual unit cells above the surface. It then follows that each of the four corner atoms will contribute $(4 \times 1/8) \times 2 = 1$ electrons to the space above the unit face, whilst the contribution from the central face atom will be $2 \times 1/2 = 1$ electron. Hence, the total number of surface valence electrons contributed by each unit cell face will be $1 + 1 = 2$ which corresponds to a surface density of valence electrons of

$$[S_{Cu}]_2 = 2 \times 7.6 \times 10^{18} = 1.5 \times 10^{19} \text{ m}^{-2}$$

and

$$[S_{Cu}]_1 = 0.76 \times 10^{19} \text{m}^-$$

If one makes a similar calculation for aluminium, with a FCC crystal structure, a lattice constant of 405pm, and a valency of 3, each unit cell face contributes a total of $[(4 \times 1/8) \times 3] + 3/2 = 3$ surface valence electrons, one has

$$[S_{Al}]_3 =. 3 \times 6.25 \times 10^{18} \text{m}^{-2} = 1.9 \times 10^{19} \text{m}^{-2.}$$
$$[S_{Al}]_2 = 1.3 \times 10^{19}$$

For silver, with a FCC crystal structure, an identical lattice constant to aluminium, and a valency of 2, each unit cell face will contribute $[(4 \times 1/8) \times 2] + 2/2] = 5/4 = 2$ surface valence electrons, so

$$[S_{Ag}]_2 = 2 \times 6.25 \times 10^{18} = 1.3 \times 10^{19} \text{ m}^{-2}$$

For nickel, with a FCC crystal structure, a lattice constant of 352pm, and a valency of 2, each unit cell face will contribute $[(4 \times 1/8) \times 2] + 2/2 = 2$

$$[S_{Ni}]_2 = 2 \times 8.3 \times 10^{18} = 1.7 \times 10^{19} \text{ m}^{-2}$$

For lead, with a FCC crystal structure, a lattice constant of 495pm, and a valency of 4, one has
$$[S_{Pb}]_4 = 4 \times 4.1 \times 10^{18} = 1.6 \times 10^{19} \text{ m}^{-2}$$
$$[S_{Pb}]_2 = 0.82 \times 10^{19}$$

For gold, with a FCC crystal structure, a lattice constant of 407pm, and a valency of 1, one has
$$[Au]_1 = 1 \times 6 \times 10^{18} \text{m}^{-2} = 0.6 \times 10^{19} \text{m}^{-2}$$

However, for niobium, which has a BCC crystal structure, with a lattice constant of 330pm, and a valency of 5, each unit cell face will contribute $[(4 \times 1/8) \times 5] = 2.5$ electrons to the population of surface valency electrons, and so

$$[S_{Nb}]_5 = 2.5 \times 9 \times 10^{18.} = 2.3 \times 10^{19} \text{ m}^{-2}$$
$$[S_{Nb}]_3 = 1.9 \times 10^{19}$$
$$[S_{Nb}]_2 = 0.9 \times 10^{19}$$

For Tantalum with a BCC crystal structure (i.e. opposed to its alternative TETRA structure) an identical lattice constant of 330pm to that of niobium, and valency of 5, one has an identical value of S_{Ta}, namely

$$[S_{Ta}]_5 = 2.3 \text{ x } 10^{19}\text{m}^{-2}$$
$$[S_{Ta}]_2 = 0.92 \text{ x } 10^{19}$$

For Tungsten with a BCC crystal structure, a lattice constant of 316pm, and a quoted valency of 6, one has

$$[S_W]_6 = 3 \text{ x } 1.0 \text{ x}10^{-19} = 3 \text{ x } 10^{19}\text{m}^{-2}$$
$$[S_W]_2 = 1.0 \text{ x } 10^{19}\text{m}^{-2}$$

A similar analysis can be made for tetravalent titanium having a close packed HCP hexagonal crystal structure with lattice constants of (295,295,468)pm. Thus, for the hexagonal 0001 crystal face, one finds that the cross-sectional area of each hexagonal face of a unit cell has an area of $(3\sqrt{3}/2)a^2$, corresponding to a numerical value of $2.2 \text{ x } 10^{-19}\text{m}^2$, so that the number of unit cells per unit area intersecting the surface is $4.5 \text{ x } 10^{18}$. For an HCP close-packed structure, it can be assumed that each of the six corner atoms will be shared between six neighbouring unit cells, and contribute one-sixth of its valence electrons to each unit cell area, whilst the central atom will contribute half of its valance electrons to the surface population. It follows therefore that the total number of surface valence electrons per unit cell will be [(6 x 1/6) x 4 + (1 x 1/2) x4] = 6. Hence, the surface density of valence electrons will be

$$[S_{Ti}]_4 = 6 \text{ x } 4.3 \text{ x } 10^{18}\text{m}^{-2} = 2.6 \text{ x } 10^{19} \text{ m}^{-2}$$
$$[S_{Ti}]_2 = 1.3 \text{ x } 10^{19}$$

Zirconium also has an HCP crystal structure with lattice constants of (323,323,514)pm, and a valency of 4, which gives

$$S_{Zr}]_4 = 6 \text{ x } 0.38 \text{ x } 10^{19} = 2.3 \text{ x } 10^{19}\text{m}^{-2.}$$
$$[S_{Zr}]_2 = 1.2 \text{ x } 10^{19}$$

Zinc is another element that has an HCP crystal structure with lattice constants of (266,266, 495) but, unlike titanium, it has a valency of 2. As a consequence it could be predicted to have a lower density of surface valence electrons which, after following a similar calculation to that above, is found to have a value

$$[S_{Zn}]_2 = 3 \text{ x } 0.7 \text{ x } 10^{19}\text{m}^{-2.} = 2.1 \text{ x } 10^{19}\text{m}^{-2}$$

The above data will now be used to investigate if there is a correlation between the surface density of valence electrons S, and the surface-dependent electronic properties of metals, in particular, the work function ø.

4. Dependency of ø on S

The above data will now be used to investigate if there is a correlation between the surface density of valence electrons S, and the surface-dependent electronic properties of metals, in particular, the work function ø. Thus, it will be seen from Figure 3 below that, when crystal-structure is taken into account, and the individually calculated S-values for the same group of metals used for the earlier model of Figure 1, are plotted against the same mean work function values, one obtains the plot of Figure 3, which clearly shows that this more refined model predicts that there is in fact a linear dependence of ø on S.

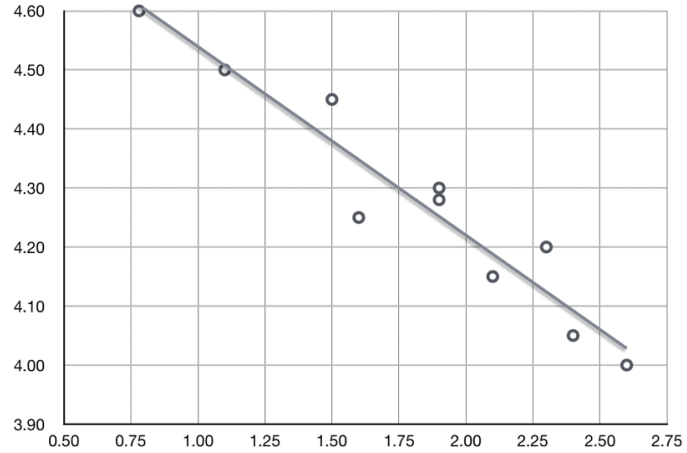| Metal	Surface Density of Valence Electrons S x 10+19	Work Function Ø (eV)
Ag(2)	0.78	4.6
Al(3)	1.9	4.28
Cu(2)	1.5	4.45
Nb(3)	1.9	4.3
Ni(2)	1.1	4.5
Ti(4)	2.6	4.0
Zr(4)	2.4	4.05
Ta(5)	2.3	4.2
Zn(2)	2.1	4.15
Pb(4)	1.6	4.25

Figure 3

The scatter in the above data points can be attributed to two uncertainties. Firstly, the quoted values for work function show a wide uncertainty, depending on the method of measurement and the atomic conditions of the surface being studied. Thus, measurements made under ambient air conditions will be measure the work function of the ambient oxide of the metal under test, as opposed to the absolute value that would be obtained under ultra clean UHV conditions. Secondly, the effective valency value of a metal frequently shows a wide variation depending on the nature of its chemical bonding, i.e. as was highlighted earlier in the case of $[Cu]_1$ and $[Cu]_2$. Hence, it is difficult to know what the appropriate value to use when analysing the passive physical regimes that are of interest to the present discussion. In this context, it is important to note that most transition metals have an electron configuration that is ns2(n−1)d in which there two ns2 outer orbital valence electrons. To investigate whether in fact it is only these two valance electrons that are operative in a physical as opposed to chemical regime, a plot of mean ø-values versus the corresponding S-values calculated by assuming a valency of 2 for all metals, results in a random scatter of data points from which one can conclude that this is in fact a false assumption. However, if one considers the case of tungsten, having quoted values 4.55eV for its work function and 6 for its valency, corresponding to an S-value of 3 x $10^{19}m^2$, its data point on the plot of Figure 3 would be way off-trend. If instead, a valency value of 3 is assumed for the present physical regime, the S-value becomes 1.5 x $10^{19}m^{-2}$, and the corresponding data point on the plot of Figure 2 lies within the bound of the general scatter.

Returning to Figure 3, it follows that the linear dependency of ø on S can be represented by an expression of the form

$$\phi = \phi_0 - k_\phi S \qquad \text{--- -----------------------(2a)}$$

where ϕ is measured in electron volts and S in m^{-2} x 10^{19}, with

$$\phi_0 = 4.85 \qquad \text{------------------------------------(2b)}$$

and

$$k_\phi = 0.3 \qquad \text{-------------------------------------- (2c)}$$

As an example of its practical application, the above analysis can be used to obtain an alternative structurally-based expression for the contact potential difference V_{CPD} between a pair of metal conductors with respective work functions of ϕ_1 and ϕ_2 , where traditionally

$$V_{CPD} = \Delta\phi/e = (\phi_1 - \phi_2)/e \text{ ----------------------------(3)}$$

However, from equation 2a above, one has

$$\Delta\phi = \phi_1 - \phi_2 = (4.7 - 0.3S_1) - (4.7 - 0.3S_2)$$
$$= 0.3(S_2 - S_1)$$

so that finally

$$V_{CPD} = \Delta\phi/e = 0.3(S_2 - S_1)/e \text{ ------------------------(4)}$$

Thus, for the example of a copper-zinc junction, equation 4 predicts a CPD of 0.22V compared with 0.25V given by the difference in the measured values of their quoted work functions.

It will also be seen from Figure 4 below, that there is another surface-related parameter, namely the electrochemical potential μ, that exhibits an approximately linear dependence on the S-value, where

$$\mu = \mu_o - k_\mu S \text{ --(5a)}$$

with

$$\mu_o = 1.25 \pm 0.2 \text{ --------------------------------------(5b)}$$
$$k_\mu = 0.97 \pm 0.2 \text{ ---------- ---------------------------(5c)}$$

It follows that the emf of any electrochemical cell $\Delta\mu$ will be given by

$$\Delta\mu = 0.97\Delta S = 0.97(S_1 - S_2) \text{ ------------------------(6)}$$

It is also important to note that a hydrogen single cell, corresponding to $\mu = 0$, has an S-value given by

$$S_{\mu=0} = S_E = 1.25 \text{ --------------------(7)}$$

which, by definition, can be identified with the value of S_E of the Earth, which is also assumed to be at zero potential.

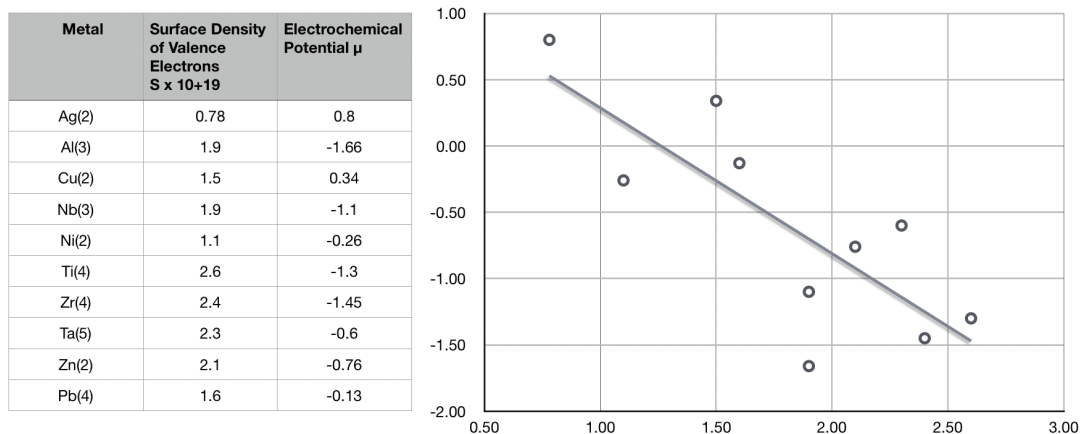| Metal	Surface Density of Valence Electrons S x 10+19	Electrochemical Potential μ
Ag(2)	0.78	0.8
Al(3)	1.9	-1.66
Cu(2)	1.5	0.34
Nb(3)	1.9	-1.1
Ni(2)	1.1	-0.26
Ti(4)	2.6	-1.3
Zr(4)	2.4	-1.45
Ta(5)	2.3	-0.6
Zn(2)	2.1	-0.76
Pb(4)	1.6	-0.13

Figure 4

5. Threshold Field for Cold Electron Emission

The cold emission of electrons from extended metal surfaces at anomalously low fields of ~100MV/m has been extensively researched in relation to its critical relevance to the performance of a wide range of practical devices, including travelling wave tubes, vacuum capacitors, vacuum switches, and particle accelerators[6]. All such devises share the need to sustain a high electric field acting on a metal electrode surface without the onset of field-induced electron emission which is assumed to be responsible for triggering the formation of a spark and subsequent electrical breakdown [7]. The main forum for reporting on-going research in this field is the two-yearly meetings of the International Symposium on Discharges and Electrical Insulation in Vacuum (ISDEIV).

From an historical perspective, this emission was found to be associated with microscopically localised sites involving "foreign" impurity grains such as carbon, that are embedded in an electrode surface and are able to promote a complex solid-state based parasitic emission mechanism that severely limits the performance of practical devices[13,14,15]. In particular, it meant that it was virtually impossible to achieve any reproducible consistency in performance. As a consequence, recent decades have seen a major technological effort to develop clean-room electrode preparation and assembly procedures, improved vacuum conditions, and in situ electrode surface treatments, all of which contribute to the elimination of electrode contamination. It is in this context that Batrakov's group recently published a seminal experimental data set showing how the d-c pulsed field dielectric strength of a vacuum gap varies with different electrode materials, and how this behaviour is related to both the work function of the electrode material and its crystal structure [9]. The data showed that there is an almost inverse linear relationship between the breakdown field E_{BF} and the work function ø of the electrode material. Also, that the highest breakdown fields are associated with materials having a close-packed HCP crystal structure, with titanium providing the best performance. This study also revealed that when using atomically pure and clean electrodes, the first breakdown event was associated with a non-localised field emission process that is characteristic of the electronic properties of the cathode surface.

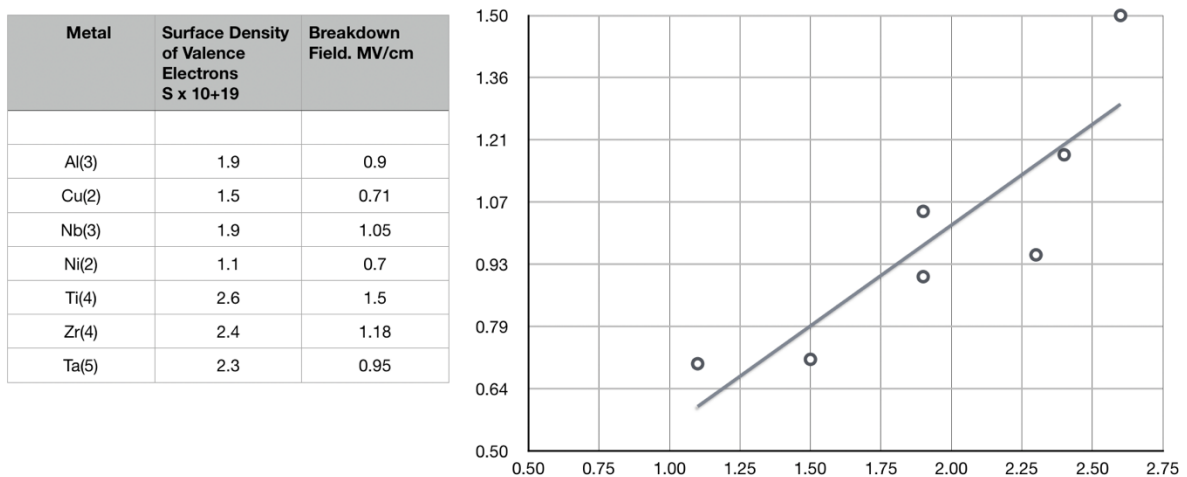| Metal	Surface Density of Valence Electrons S x 10+19	Breakdown Field. MV/cm
Al(3)	1.9	0.9
Cu(2)	1.5	0.71
Nb(3)	1.9	1.05
Ni(2)	1.1	0.7
Ti(4)	2.6	1.5
Zr(4)	2.4	1.18
Ta(5)	2.3	0.95

Figure 5

In relation to the analysis of the present paper, it is of interest to determine if there is a relationship between the S-value of an electrode material and the threshold field for electron emission and associated breakdown strength. Thus, in Figure5 above, the mean breakdown field values E_{BF} taken from the data set referred to above [9] have been plotted against the

corresponding S-values of the electrode material, and reveals that there is in fact a positive linear relation between E_{BF} and S. The considerable scatter of the data points in this plot is partly due to the uncertainty in the choice of valency when calculating the S-values, and partly due to the error bars in the measured E_{BF}-values [9]. Nevertheless, the above plot clearly illustrates that a high S-value, and associated low work function, are key requirements of a material that is required to support a high threshold field for the cold emission of electrons.

6. Discussion

The central challenge arising from the above analysis is to explain how the mean S-value of an ideal crystalline surface has such a contrasting influence on the photon energy threshold for the photoelectric emission of electrons (Figure 3), and the threshold external field of ~10^8V/m required for their cold emission (Figure 5). So, whilst a detailed quantitative analysis of these issues is beyond the scope of the present investigation, it is possible to explore if a qualitative approach can provide explanations for the behaviour of the two phenomena.

6.1 Dependence of Ø on S

Hence, in the case of why a high S-value is associated with a low work function, it can be assumed that the surface population of S-electrons will behave as a quantised electron gas, i.e. as in the bulk, and hence will have its own energy distribution. It follows therefore that, the higher the population density of electrons, i.e. the S-value, the higher will be the associated Fermi energy, and hence the lower the work function and consequent lower minimum photon energy required to emit an electron.

6.2 Dependence of E_{BF} on S

In seeking an explanation for this dependence, it firstly has to be recognised that there is an entirely different emission mechanism operating under high field conditions compared with that of photoemission. Thus, the field-induced, or "cold", emission of electrons has traditionally been studied using a point-plane electrode geometry where the field has to be geometrically enhanced at the point-cathode to a threshold value of >10^9 V/m, in order for the Fowler-Nordheim (F-N) quantum mechanical tunnelling mechanism to operate [6]. In contrast, the threshold field for "cold" emission with planar electrodes is over an order of magnitude lower, which suggests that electrons are not being emitted by the F-N quantum tunnelling mechanism as originally proposed. It is therefore necessary to investigate if the net electro-mechanical force acting on an field-induced s-electron field is sufficient to release it from the cathode surface.

In pursuing this perspective, it has firstly to be recognised that the density of surface-induced s-electrons at a field of 10^7V/m has a value of 6 x 10^{15} m^{-2}. In practical terms, this corresponds to a very sparse population, with each induced s-electron "occupying" a mean area of ~10^2nm^2 which, if it is assumed that the typical surface area of a unit cell is ~0.25nm square, corresponds to 1600 unit cell faces, or a matrix of 40 x 40 unit cells. This implies that there will be a sparsely distributed "spikey" potential distribution across the electrode surface; i.e. quite unlike the uniform potential distribution assumed by the Fowler-Nordheim theory. If it is now assumed that the applied field acts separately on each individually isolated

s-electron, one has to enquire into the balance of forces acting on an s-electron, and the associated threshold condition for an electron to escape from the surface.

Thus, as discussed by Mastwijk et al [4], under zero-field conditions, an S-electron experiences a net attraction to the cathode surface under the influence of three intrinsic forces, namely, (i) the coulomb attractive force between the electron and the ion cores of the surface atoms F_1, (ii) the repulsive force between the electron and the population of neighbouring surface electrons F_2, and (iii) an attractive quantum mechanical spin coupling force F_3. Under high-field conditions, an isolated s-electron will be subject to two additional and oppositely-directed forces; namely, the force F_4 exerted by the applied field , and the image force F_5 . It follows that the necessary condition for an s-electron to be "cold" emitted from the cathode is

$$F_2 + F_4 > F_1 + F_3 + F_5 \text{ ---------------------------(8)}$$

where it should be noted that both F_4 and F_5 would not feature in the photoemission process.

In considering how this inequality is influenced in the contrasting cases of copper and titanium cathodes, it can firstly be assumed that, under identical field conditions, both F_4 and F_5 will have the same value for each material. Hence if this explanation for the differing insulating performance of Cu and Ti is valid, the following inequality has to be satisfied

$$[F_1 + F_3 - F_2]_{Ti} > [F_1 + F_3 - F_2]_{Cu} \text{ --------------------(9)}$$

As to the relative values of these forces, it can be assumed that F_1 will be significantly larger in the case of titanium due to a) its higher valency, and hence higher positive charge on the Ti ions, and b) its close-packed crystal structure and its associated smaller lattice constant. In contrast, the repulsive force F_2 on an isolated s-electron will be higher in the case of Ti due to the presence of its higher density of surface S-electrons This same condition can be expected to result in a significantly higher value of the attractive force F_3 with Ti as opposed to Cu. Since however, a quantitative evaluation of these forces is beyond the scope of the present analysis, it remains an open question as to whether this model provides an explanation of the experimentally observes ehaviour.

Finally, the possibility of the anode having an influence on the emission process must not be excluded [7] until it has been experimentally checked that the use of a say a copper anode has no influence on the performance of a titanium cathode. It would also be of interest to investigate if there are other possible electrode materials with a lower S-value than titanium which, according to the prediction of Figure 5, could potentially support even higher surface threshold fields.

6. Conclusion

Although only a first-order analysis, with significant error bars in the data points, its findings are sufficiently indicative to warrant future verification and a more detailed theoretical analysis. Of particular significance is the physical role played by the S-parameter in determining the surface properties of a metal, with particular reference to why a high S-value promotes the photo emission of electrons, but suppresses their field emission. The findings could also have important practical implications, in that the S-value could be used as an aid

when choosing the material for a specific surface-related technological application; i.e. rather than having to make trial and error practical measurements.

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