Concerning the Theory of the Surface Tension of Metals

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Title: Concerning the theory of the surface tension of metals. (K teorii poverkhnostnogo natyazheniya metallov.)

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The Theory of the Surface Tension of Metals

According to the theory of the surface tension of metals proposed by A. E. Glauberman (1), the latter is determined as an excess energy of the lattice per unit of surface, brought about by the presence of a boundary. The kinetic energy of an electron gas introduces a negative correction, equal in magnitude to one-half of the electrostatic portion of the surface tension, which is in complete agreement with the virial theorem.

A. E. Glauberman carried out calculations of the surface tension for two types of metallic lattice: the space-centered and the face-centered. A calculation is proposed in the present note for a hexagonal, closely packed system which includes all the metallic structures. The calculation is carried out first for point ions, and then a correction is introduced for their volumes.

The Electrostatic Potential.

We will imagine the whole lattice as being subdivided into two portions by the plane $z = 0$. We will determine the electrostatic potential of the half lattice φ_a in the semispace which is external to it. For this purpose we will take an elementary nucleus consisting of two ions, surrounded by an electron "liquid", and we will select a system of co-ordinates as indicated in the Figure.

The angle xoy is equal to 60°, the angles xoz and yoz are right-angles. The dimensions of the nucleus with respect to the axes ox, oy are equal to the base of the nucleus a; with respect to the axis oz it is equal to c, moreover, since the packing is then approximately $\frac{c}{a} = 1.63$.

The co-ordinates of the ions of the "zero" nucleus are

$$X_1 = -\frac{a}{6}, \quad Y_1 = -\frac{a}{6}, \quad Z_1 = -\frac{3}{4}c,$$

$$X_2 = \frac{a}{6}, \quad Y_2 = \frac{a}{6}, \quad Z_2 = -\frac{1}{4}c.$$

The centre of the "zero" nucleus is displaced by half C along the OZ axis in relation to the origin.

We will express the density of the electric charge of the lattice ρ by a Fourier series without the zero term (2)

$$\rho = \sum_{l,m,n=-\infty}^{\infty}{}' \rho^{+}_{lmn} e^{2\pi i\left(\frac{lx}{a} + \frac{my}{a} + \frac{n(z+\frac{c}{2})}{c}\right)}. \quad (1)$$

The Fourier coefficients ρ^{+}_{lmn} are determined

$$\rho^{+}_{lmn} \begin{cases} = \frac{2l}{a^2 c}\left[(-1)^{\frac{n}{2}} \left|\cos\frac{\pi}{3}(l+m)\right|\right] & \text{for n even} \\ = \frac{2l}{a^2 c}\left[(-1)^{\frac{n+1}{2}} \sin\frac{\pi}{3}(l+m)\right] & \text{for n odd} \end{cases} \quad (2)$$

The potential φ_a, which satisfies the Laplace equation

$$\nabla^2 \varphi_a = 0, \tag{3}$$

we will express in the form:

$$\varphi_a = \sum_{\ell,m=-\infty}^{\infty} f(z) \cdot e^{\frac{2\pi i}{a}(\ell x + m y)} \tag{4}$$

The Laplace operator in our system of co-ordinates has the form

$$\nabla^2 = \frac{3}{4}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} - \frac{\partial^2}{\partial x\, \partial y}\right) + \frac{\partial^2}{\partial z^2} \tag{5}$$

substituting (4) into 3), we obtain the equation for $f(z)$, the solution of which is

$$f(z)_{\ell m} = C_{\ell m} e^{-x_{\ell m} z} \qquad (z > 0), \tag{6}$$

where

$$x_{\ell m} = \frac{2\pi}{a}\sqrt{\ell^2 + m^2} - \ell m.$$

Inside of a semi-infinite lattice the electrostatic potential φ_i, which may be expressed in the form

$$\varphi_i = \sum_{\ell,m=-\infty}^{\infty} g(z) \cdot e^{\frac{2\pi i}{a}(\ell x + m y)}, \tag{7}$$

satisfies the Poisson equation

$$\nabla^2 \varphi_i = - 4\pi\rho, \qquad (8)$$

which provides the possibility of obtaining a solution for g (z) in the form:

$$g(z) = M_{\ell m} e^{x_{\ell m} z} + \sum_{n=-\infty}^{\infty} \frac{4\pi\rho^{+}_{\ell mn}}{x^2_{\ell m} + \frac{4\pi^2}{c^2} n^2}, \quad (z < 0) \qquad (9)$$

Making use of the boundary condition for the potential at Z = 0 $\varphi_i = \varphi_a$ and $\frac{\partial \varphi i}{\partial z} = \frac{\partial \varphi a}{\partial z}$,

we will determine the coefficients $C_{\ell m}$

$$C_{\ell m} = \frac{2\pi e}{a^2 x_{\ell m}} \left[\frac{\cos\frac{\pi}{3}(\ell + m)}{e^{x_{\ell m}\frac{c}{4}} - e^{-x_{\ell m}\frac{c}{4}}} - i \frac{\sin\frac{\pi}{3}(\ell + m)}{e^{x_{\ell m}\frac{c}{4}} + e^{-x_{\ell m}\frac{c}{4}}} \right]. \qquad (10)$$

Separating the real part of φ_a, we will obtain the expression

$$\varphi_a = \frac{2\pi e}{a^2} \sum_{\ell, m=-\infty}^{\infty}{}' \left[\frac{\cos\frac{\pi}{3}(\ell+m) \cdot \cos\frac{2\pi}{a}(\ell x + m y)}{x_{\ell m}\left(e^{x_{\ell m}\frac{c}{4}} - e^{-x_{\ell m}\frac{c}{4}}\right)} \right.$$

$$\left. + \frac{\sin\frac{\pi}{3}(\ell+m) \cdot \sin\frac{2\pi}{a}(\ell x + m y)}{x_{\ell m}\left(e^{x_{\ell m}\frac{c}{4}} + e^{-x_{\ell m}\frac{c}{4}}\right)} \right] \cdot e^{-x_{\ell m} z} \qquad (11)$$

The Surface Tension.

The electrostatic portion of the surface tension is determined from (2)

$$\sigma_E = - \frac{u_{12}}{2S} , \tag{12}$$

where u_{12} is the coulombic energy of interaction of a semi-infinite crystal with a column of the second half lattice, which has a rhombus as a base, whose side is a, the acute angle is 60°, and the area $S = \frac{a^2\sqrt{3}}{2}$

$$u_{12} = \sum_k e_k \varphi_a(x_k, y_k, z_k),$$

where k is the number of the ion in the column, $e_k = e$ is the charge of the ion. Taking into account that $e^{x_{\ell m}\frac{c}{2}} \gg 1$, we obtain after calculations

$$u_{12} = \frac{2\pi e^2}{a^2} \sum_{\ell,m=-\infty}^{\infty}{}' \frac{\cos\frac{2\pi}{3}(\ell+m)}{x_{\ell m} e^{x_{\ell m}\frac{c}{2}}} . \tag{13}$$

The sum (13) can be subdivided into two portions, one of which is taken with respect to the indexes ℓ, m, for which $\ell + m$ is a multiple of three, and the other with respect to all other values of ℓ, m.

As a result of the summation and in accordance with (12) we will obtain $\sigma_E = \frac{e^2}{a^3} \cdot 0.0042$

and the total surface tension

$$\sigma = \frac{1}{2} \sigma_E = \frac{e^2}{a^3} \cdot 0.0021. \qquad (14)$$

In order to make a comparison with the experimental data, it is necessary to introduce a correction for the volume occupied by the ions, since the electron gas of a metal hardly penetrates inside the ions.

Following A. Glauberman, we will consider the "reduced" charge of the ion e' as being a point, and the electron gas as having a certain density ρ', moreover

$$\rho' = \frac{ne'}{V-V'},$$

where $n = 2$ and is the number of ionic charges per nucleus, $V = a^3\sqrt{2}$ and is the volume of the elementary nucleus, $V' = 2 \cdot \frac{4\pi}{3} R_1^3$ and is the volume occupied by the two ions of radius R_1,

$$e' = e + \frac{eV'}{V-V'} = \frac{e}{1 - \frac{8\pi}{3\sqrt{2}} \left(\frac{R_1}{a}\right)^3} \qquad (15)$$

In formula (14) the charge e should be substituted by e' in accordance with (15) and the final formula for the surface tension of metals of a hexagonal closely

packed structure is

$$\sigma = \frac{e^2}{a^3\left[1 - \frac{8\pi}{3\sqrt{2}}\left(\frac{h_1}{a}\right)^3\right]^2} \cdot 0.0021. \qquad (16)$$

A comparison of the calculated values for σ with the experimental is given in the table*

Metal	The Constant of the Lattice a 10^{-8} cm.	Calcul. dynes/cm.	Exper. dynes/cm.
Zn	2.66	1100	743
Cd	2.97	880	630
Mg	3.20	204	-
Ca	3.94	130	-
Co	2.505	1530	-
Ni-α	2.49	1560	-
Os	2.73	1190	-

In conclusion, the author wishes to express his thanks to A. Glauberman for his guidance in this work.

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* The charge of the ion is assumed equal to the average chemical valency of the metal.

Conclusions

1. The electrostatic potential for a metallic lattice of a hexagonal closely packed structure was found.

2. By means of this potential a calculation is made of the surface tension for metals with hexagonal closely packed structure. A comparison of the results of calculation with the existing experimental data for metals of this type Zn and Cd indicates that the theory proposed by Glauberman, in which the determining function in the value of the surface tension of a metal is fulfilled by the excess potential energy, appearing as a result of the presence of a boundary surface, gives good agreement with experiment also for metals of the hexagonal densely packed structure, which completes the analysis of the problem for all metallic structures.

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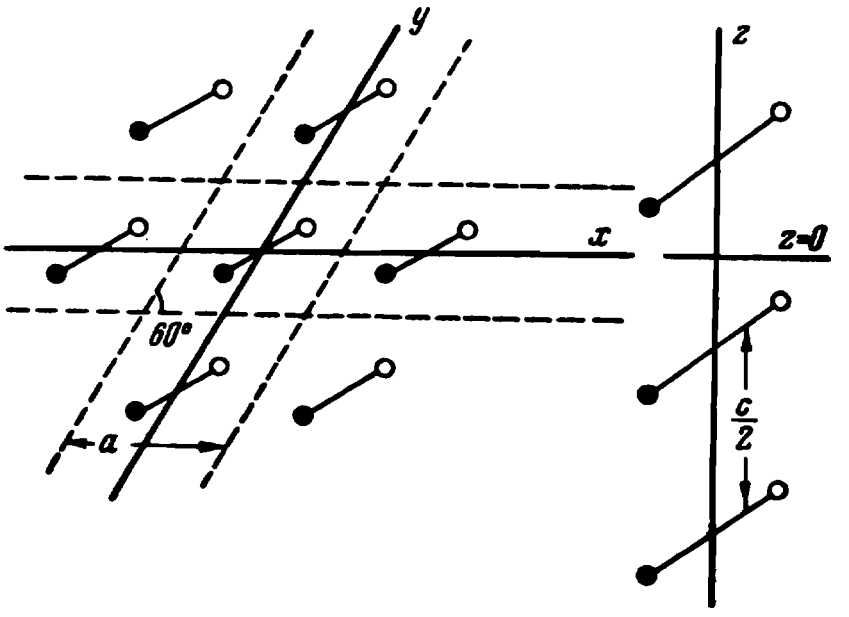
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