On the Influence of Dispersion on the Electron Work Function

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It is known that the chemical potential of a component of a solution contains the term

$$\frac{2\sigma\bar{v}_i}{r} \tag{1}$$

(σ is the surface tension, $\bar{v}_i$ is the partial volume, r is the radius of the meniscus), which describes the influence of dispersion on thermodynamic properties. It is of interest to solve an analogous problem for electrons in a metal, i.e., to determine the dependence of the electron work function φ on the size of the body, which determines a number of important properties and processes. Above all this applies to the distribution of local charges in the bulk and on the surface of a real solid. The boundaries of blocks and grains, microcracks, dislocations, and other defects contain definite charges. It is known that the presence of charge lowers the surface tension and substantially affects mechanical properties. An accumulation of charge must determine the horophilicity of elements, the association of an impurity cloud with a dislocation, diffusion along short-circuit paths, the processes of formation of nuclei during crystallization of a new phase, and also influence the processes of adsorption and catalysis. Finally, the indicated dependence probably is also connected with the question of the reproducibility of the results of measurements of φ.

Here we consider a simple theory of the dependence of φ on the size of the body and present some experimental data arising from this dependence.

The effect described by formula (1) is due to a change in surface energy upon removal of 1 mole of a component. When electrons are removed, the surface of the body practically does not change. However, an effect analogous to (1) arises for electrons because the energy of the electron gas depends substantially on the magnitude of the surface. Upon dispersion of a metal, the energy of the electrons increases, which accounts for a substantial part of the surface tension. The increase in kinetic energy leads to a decrease in φ. Following the method developed by one of the authors with A. Kh. Berger ([1]), we shall consider the simplest model of a metal—the potential-box model, in which the only quantity under discussion is the kinetic energy of the electron gas.

As in ([1]), let us consider this quantity for a metallic cube with edge equal to a. If the lattice period is Δ, then the body contains N^3 electrons, where $N = a/\Delta$.

The kinetic energy of the electron gas E is determined as the sum of the energies of all electrons, i.e., $E = 2\sum E_{l,n,p}$. Here

$$E_{l,n,p} = \frac{h^2}{8ma^2}\left(l^2 + n^2 + p^2\right).$$

The summation must be carried out over the $N^3/2$ lowest allowed levels.

Thus,

$$E = \frac{2\alpha}{N^2}\sum_{N^3/2}(l^2 + n^2 + p^2),$$

where $\alpha = h^2/8m\Delta^2$.

If the summation is carried out and terms of lower order relative to N are neglected, then, according to ([1]), the expression for the energy takes the form

$$E = \frac{\pi b^5}{5}N^3 + \frac{3\pi b^4}{8}N^2,$$

where $b = \sqrt[3]{3/\pi}$.

The second term of the equation corresponds to the surface energy. We are interested in the change in the energy of the gas when one electron is removed, i.e. $\Delta E = (E - E_2)/2$, where E_2 is the energy of an electron gas containing, in the same volume a^3, two fewer electrons. E_2 is calculated analogously, but the summation is carried out over $N^3/2-1$ levels. After summation, neglecting the square of the small quantity $1/N^3$, we obtain

$$E_2 = \alpha\left[\frac{\pi b^5}{5}N^3\left(1 - \frac{10}{3N^3}\right) + \frac{3\pi b^4}{8}N^2\left(1 - \frac{8}{3N^3}\right)\right].$$

Hence

$$\Delta E = \alpha\left[\frac{\pi b^5}{3} + \frac{\pi b^4}{2N}\right].$$

The difference in the work function $\Delta\varphi$ of a small cube as compared with an infinitely large one is equal to $\Delta\varphi = \Delta E(\infty) - \Delta E(N)$. Thus,

$$\Delta\varphi = -\frac{\alpha\pi b^4}{2N}.$$

It was shown ([1]) that, within the framework of the same model, $\sigma = \alpha\pi b^4/16\Delta^2$. Introducing the electron density $\rho = 1/\Delta^3$, we obtain $\Delta\varphi = -8\sigma/a\rho$, or, after introducing the radius of a sphere with the same ratio of increments of surface area and volume ($a = 2r$), we obtain

$$\Delta\varphi = -4\sigma/r\rho.$$

This formula is an analogue of formula (1) and differs from it only by the value of the numerical factor.

If one uses the equation derived in ([1]) for the surface tension

$$\sigma = \frac{h^2\pi b^4}{128m}\rho^{4/3},$$

then it is not difficult to show that $\Delta\varphi = -\pi^3 b^4 e^2/4\Delta' a = -7.3e^2/\Delta' a$ (here Δ' is the ratio of the lattice period to the radius of the first Bohr orbit), or

$$\Delta\varphi = -\frac{3.7}{\Delta'}\frac{e^2}{r}.$$

Along with this effect it is also necessary to take into account the charging energy of the small sphere, $e^2/2r$. Thus,

$$\Delta\varphi = -\frac{e^2}{r}\left(\frac{3.7}{\Delta'} - \frac{1}{2}\right).$$

Like the effect described by formula (1), the effect of the change in φ will manifest itself only for small r. Thus, for molybdenum ($\Delta' = 5.4$) at $r = 10^{-6}$ cm we obtain $\Delta\varphi = 0.03$ eV.

A direct verification of the equations obtained encounters serious methodological difficulties. However, some experimental facts can be interpreted on the basis of the considerations given above. Thus, in ([2]) it was established that φ of freshly evaporated Au and Ag films in vacuum is lower than φ of massive specimens. During plastic deformation, dislocations and slip planes emerge at the surface, increas-

the micro-roughness of the surface increases, and the mosaic blocks are fragmented. It should be expected that, as a result of these processes, φ will decrease.

Indeed, in experiments with various metals it was found that deformation causes an increase in photoelectron and secondary electron emission[3,4]. The change in φ under plastic deformation may also be caused by partial renewal of the surface, if the surface

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

Fig. 1

for some reason had been poorly cleaned of adsorbed gases. If it is assumed that the microinhomogeneities that form do not adsorb gas molecules, then, at a sufficiently low vacuum, the effect of deformation on φ should disappear after an appropriate holding time. The purpose of the experiments we carried out was to prove the influence of deformation on φ and to determine the stability of the effect after deformation was stopped.

Measurements were made of the contact potential difference between two single-crystal molybdenum filaments ($d = 50\,\mu$), one of which was deformed with the aid of a solenoid. The measurements of the contact potential difference were performed by the vibrating-string method with an accuracy of 0.005 V.

Fig. 2

Figure 1 shows the measuring cell used in the present experiments. Here 1 is the reference filament, 2 the filament being deformed, 3 a glass-coated core, 4 an external contact with a shielding layer of evaporated Mo or Pt, and 5 a getter bulb with a tantalum getter.

Figure 2 gives experimental curves for the change in the work function $|\Delta\varphi|$ versus deformation $\Delta l/l$, obtained during continuous deformation of molybdenum filaments at a rate of 1 mm/min in a vacuum of $5\text{–}2\cdot10^{-8}$ mm Hg. To characterize reproducibility, Fig. 2 presents the results of two identical experiments. It was established that plastic deformation causes a decrease in φ of the specimen.

It should be noted that a similar effect was also observed under conditions of a lower vacuum, 10^{-4}–10^{-5} mm Hg, and for oxidized specimens. Independently of the vacuum, the value of $|\Delta\varphi|$ corresponding to a certain attained degree of deformation remained constant after deformation was stopped (at least for 2 hours).

The observed effects of a decrease in φ during deformation of the metal are consistent with the theoretical considerations presented above. However, other possible interpretations of these effects should also be taken into account. In particular, the effect may be caused by a change in the properties of films present on the surface ([5]). In addition, surface defects affect the magnitude of the surface step due to the smearing of electron wave functions outside the metal ([6]). Changes in the adsorption conditions of gas molecules, associated with the appearance of microcracks and protrusions, may also be reflected in φ.

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Note: Figure translations are in progress. See original paper for figures.