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SUPERFICIAL TENSION OF PURE METALS

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In work questions of experimental definition of a superficial tension of massive samples and nanoparticles pure metals are considered. The model allowing with good accuracy to define size of a superficial tension, its dependence on temperature and on the size of particles is offered. Results of calculations are compared to known models and a method of "zero creep».

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Experimental definition of a superficial tension of solid states is complicated by that their molecules (atoms) are deprived possibility freely to move. The exception makes a plastic current of metals at the temperatures close to a melting point [1].

Recently we had been offered methods of experimental definition of a superficial tension of solid dielectrics and the magnetic materials, based on universal dependence of physical properties of solid state on its sizes [2-4]. In this work we spend comparison of our method with a method of «zero creep».

A method of «zero creep» the sample (a long thread, a foil) heat up to enough heat so it starts to be reduced on length under the influence of superficial pressure. The external force is put to the sample, supporting invariable the form of the sample. On size of this force define size of a superficial tension. Experimental data for some metals are taken [5] from work and are resulted in table 1.

Table 1. Experimental on a superficial tension of some metals and their comparison with our method

Metal	Temperature, ºC	σ, j/m2 [5] (solid phase)	σ, j/m2 (our method)	σ, j/m2 [1] (liquid phase)
Ag	930	1,14 ± 0,09	-	0,126
Al	180	1,14 ± 0,2	1,070	0,093
Au	1040	1,37 ± 0,15	1,312	0,132
Cu	900	1,75 ± 0,09	-	0,177
Pt	1310	2,3 ± 0,8	-	0,208
W	1750	2,9 ± 0,3	-	-
Zn	380	0,83	-	-

In work [6] and a number of others we receive the formula which describes dependence of physical properties of a solid state on its size:

$$A(r) = A_0 \cdot \left(1 - \frac{d}{r}\right). \quad (1)$$

Here A_0 - physical properties of the massive sample; A (r) - physical properties of a small particle or a thin film; d - critical radius or a critical thickness of a film since which dimensional effects are shown. For critical radius we receive the formula:

$$d = \frac{2\sigma\upsilon}{RT}. \quad (2)$$

Here σ - a superficial tension of the massive sample; υ – a molar volume; R - a gas constant; T - temperature.

To illustrate a method, we will result our experimental results described in work [7]. Specific magnetization of Fe_3O_4 was investigated by us on vibrating magnetometer. The size of grain of Fe_3O_4 was defined on a microscope. Results are shown in figure 1.

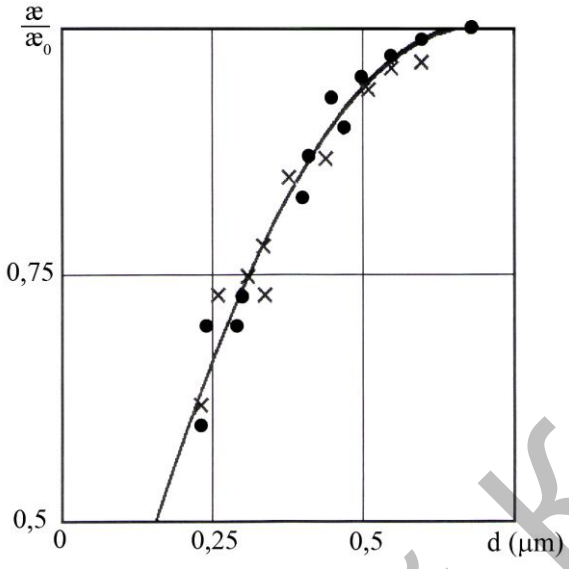

Fig. 1. Dependence of a relative magnetic susceptibility on diameter of grain of Fe_3O_4.

In coordinates $æ/æ_0$ ~1/r the experimental curve is straightened according to (1), giving value d = 0,36 μm. For a $Fe_3O_4 \cdot \upsilon$ = 44.5 sm^3/mol, and from a parity (2) for a superficial tension σ it is received: σ = 10,07·10^3 erg/sm^2. Calculation of density of superficial energy for a Fe_3O_4, spent by many authors [8], gives ω = 10,1·10^3 erg/sm^2 that coincides with the size received by us σ.

In recently left monography of the japanese and russian physicists [9] it is considered, that reduction of temperature of fusion of small particles is connected by that atoms on a surface have smaller number of neighbours, than in volume are, hence, less strong connected and less limited in the thermal movement. In the same place it is noticed, that usually temperature reduction of nanocrystals in inverse proportion to its size (fig. 2). However the theory of this effect while is not present.

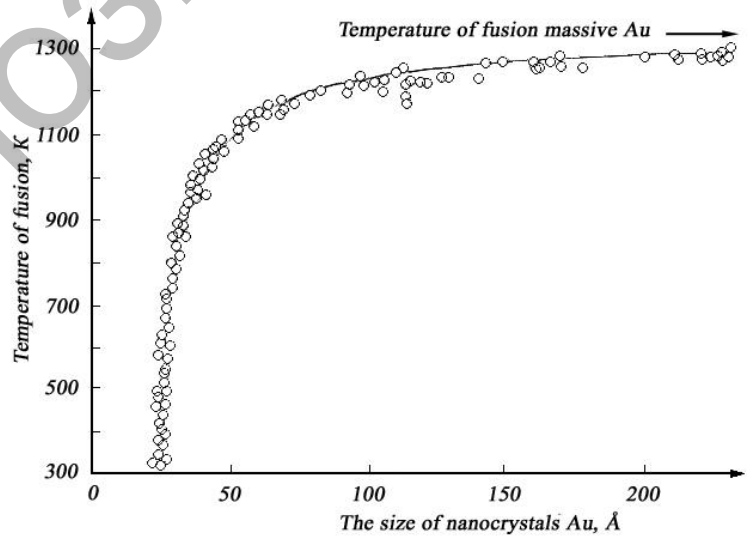

Fig. 2. Fusion temperature of nanocrystals gold as function of their size [9].

If to take advantage of analogy of scalar fields we receive the equation similar (1) for temperature of fusion of small particles:

$$T_{пл} = T_0\left(1-\frac{d}{r}\right), \quad (3)$$

where T_0 - temperature of fusion of the massive sample.

Using the experimental results shown on a figure 2, it is possible (3) to define a superficial tension of small particles of gold under our formula. At temperature T = 1040 ºC the size of a superficial tension of gold has appeared equal: σ = 1,312 j/m^2. This size slightly differs from the size of a superficial tension received in a method of «zero creep» (table 1).

In work [10] for a nanocrystals aluminium the experimental curve similar to a curve, shown on figure 2 is received. Calculation of size of a superficial tension under our formula (3) has yielded the following result: σ = 1,070 j/m^2. This size also slightly differs from the size of a superficial tension received in a method of «zero creep» (table 1).

From the formula (2) linear dependence of a superficial tension on temperature turns out:

$$\sigma = \alpha T. \quad (4)$$

Using given tables 1, it is easy to calculate factor α. Results of calculation are shown in table 2.

Table 2. Values of temperature factor α for a superficial tension of metals

Metal	α·10-3 j·m-2·K-1	Metal	α·10-3 j·m-2·K-1
Ag	0,94	Pt	1,5
Al	2,5	W	1,4
Au	1,1	Zn	1,2
Cu	1,5	-	-

If to consider an error of measurements (table 1), value of factor equally $\alpha \approx 10^{-3}$ j·m^{-2}·K^{-1} for all metals.

In work [11] linear dependence between a superficial tension and temperature of fusion of an element also is received. This dependence is illustrated in figure 3.

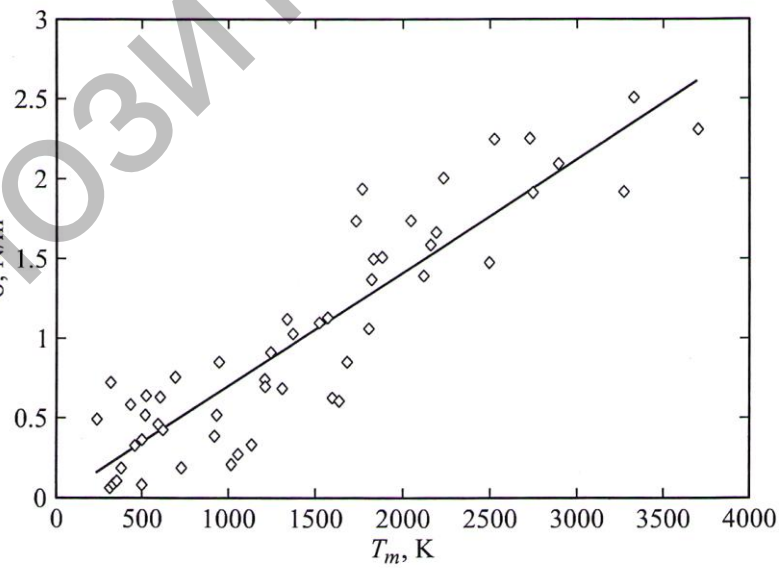

Fig. 3. Correlation dependence of a superficial tension on temperature of fusion [11].

In this figure experimental data for 54 elements of a periodic table of Mendeleyev, taken of [12, 13], and a straight line - calculation under the formula are designated

$$\sigma = 0{,}702 \cdot 10^{-3} T_m, \quad (5)$$

where the numerical factor is received by a method of the statistical analysis. The proportionality factor in the formula (5) matters close received by us.

Thus, the estimation of a superficial tension of metals can be made on their temperature of fusion and factor $\alpha \approx 10^{-3}$ j·m^{-2}·K^{-1} under the formula (4).

From table 1 follows, that in a liquid phase of metals the superficial tension decreases for all metals approximately in 10 times.

Bases of thermodynamics of curvilinear borders of section have been put in pawn still J. Gibbs [14]. Then R. Tolmen and its followers have reduced this problem to the account of dimensional dependence of a superficial tension (see, for example, [15]).

In 1949 R.Tolmen has deduced the equation for a superficial tension σ:

$$\sigma / \sigma_\infty = (1 + 2\delta / R_s)^{-1} \quad (6)$$

Here σ_∞ - a superficial tension for a flat surface; R_s - radius of a surface of a tension; $\delta > 0$ - distance between the molecular a dividing surface and a surface of a tension for flat border.

The order of size of parameter δ, named constant of Tolmen, should be comparable with effective molecular diameter. $At \cdot R >> \delta$ formula of Tolmen can be copied in a kind:

$$\sigma / \sigma_\infty = 1 - 2\delta / R. \quad (7)$$

Thus, approach of Tolmen is reduced to the amendment account on curvature of a surface to macroscopical value of a superficial tension σ_∞. It is necessary to notice what experimentally to define constant of Tolmen it is not obviously possible.

For small R A.I.Rusanov [16] has received linear dependence:

$$\sigma = KR. \quad (8)$$

Here K - proportionality factor. The formula (8) is received on the basis of thermodynamic consideration and should be applicable to small objects of the various nature. However, borders of applicability of the formula (8) and values of parameter K remain till now practically not investigated.

Within the limits of our model (the formula 1 and 2) for K easy to receive:

$$K = \frac{RT}{2\vartheta} \cdot \left(1 + \frac{A(r)}{A_0}\right). \quad (9)$$

Here A_0 - the measured physical size of the massive sample; ϑ - the molar volume; T - temperature; R - a gas constant. Formulas 1 and 2 are thus true:

$$A(r) = A_0\left(1 - \frac{d}{r}\right). \qquad d = \frac{2\sigma\vartheta}{RT}. \quad (10)$$

The criterion of applicability of the formula of Rusanov A.I. will be expressed in a kind (table 3).

$$r_k \geq d = \frac{2\sigma\vartheta}{RT} \quad (11)$$

Table 3. Criterion of applicability of the linear formula of A.I.Rusanov

Metal	r_k, nm	Metal	r_k, nm
Pb	0,9	Ag	1,1
Sn	0,8	Au	1,1
Fe	1,2	Cu	1,0

From table 3 it is visible, that for all metals r_k has size about 1 nanometer. Surprisingly, but the same order has the critical size r_k a germ at formation of crystals.

Let's notice also, that constant of Tolmen is equal in our model $\delta = r_k/2 \approx 0{,}5$ nanometers. If to take advantage of an analogy method, it is possible to receive the formula of type (1) or (7):

$$\sigma(r) = \sigma_0\left(1 - \frac{r_k}{r}\right). \qquad (12)$$

Using the formula (11), it is possible to calculate r_k. Then using given tables (1) and the formula (12), we calculate value of a superficial tension of particles in the size 2 and 10 nanometers. Results for some metals at T = 300 K are presented in table 4.

Table 4. The superficial tension of particles some metals

Metal	T, K	σ(r), r =2 nm (j/m2)	σ(r), r =10 nm (j/m2)
Ag	300	0,155	0,257
Au	300	0,198	0,304
Cu	300	0,180	0,396

From table 4 it is visible, that already at the size of particles 10 nanometers size of a superficial tension there are more comes nearer to size of a superficial tension of the massive sample (see, table (1).

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