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To cite this article: E N Eremin *et al* 2017 *J. Phys.: Conf. Ser.* **858** 012010

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Universal size dependence of the physical properties of nanomaterials

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Abstract. Dimensional analysis of the experimentally observed dependence of the physical properties of nanoparticles, nanofilms and nanomaterials showed that there is a universal equation that accurately describes the observed size effects. It is shown that the size factor is also a universal value and is determined only by the atomic structure of the nanomaterial. Discovered universal relationships enable us to calculate the physical properties (mechanical, electrical, magnetic, thermal, etc.) of small particles and thin films based on knowledge of the properties of bulk materials.

1. Introduction

A characteristic feature of the nanoparticles and nanomaterials is the size dependence of their physical properties. To distinguish two types of size effects [1]: own, or internal, associated with changes in properties such as melting temperature, heat capacity, and others, and the external, which is the size-dependent response to the external action of the forces that are independent of the internal effect (electric conductivity, magnetic susceptibility, and others).

2. Formulation of the problem

Currently there is no quantitative theory that allows to predict the desired properties of nanomaterials depending on the technological conditions. Therefore, even high quality models may help to avoid a large amount of routine, but expensive works.

In this paper we want to show that most of both internal and external dimensional effects described by one universal dependence. This makes it possible to calculate the physical properties (mechanical, electrical, magnetic, thermal, etc.) of small particles and thin films based on knowledge of the properties of bulk materials.

3. Theory

The physical nature of reducing the melting point of the particles with decreasing size is as follows: with a decrease in particle size increases the proportion of surface atoms, which is less than the binding energy of atoms than in volume, so that less energy is required for the thermal motion of the phase transition solid-liquid. However, to find a quantitative relation between the melting point of the nanoparticles and their size was not easy [2]. The melting point of the most accurate for the gold



nanoparticle size dependence was defined in the pioneering work [3]. A similar relationship was observed by many authors later for some other metal nanoparticles.

It was found that the experimental curves are well described by the equation [4]:

$$T_m(r) = T_\infty \left(1 - \frac{d}{r} \right), \quad (1)$$

where T_∞ - the melting point of the bulk sample.

The parameter d is determined by the formula [4]:

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

Here σ - the surface tension of the bulk sample; v - molar volume, R - universal gas constant.

When $r < d$, instead of (1) need to use the equation:

$$T_m(r) = T_\infty \left(1 - \frac{d}{d+r} \right). \quad (3)$$

Equation (1) allows you to experimentally determine the surface tension of the solid-state σ [5].

Processing of the experimental curves by means of (1) has shown that for metals with great precision the relation:

$$\sigma = 0,7 \cdot 10^{-3} \cdot T_\infty. \quad (4)$$

In other words, between the value of the surface tension and pure metal melting point there is a simple universal dependence (4). Note that the relationship (4) was also obtained in [6] in another way.

When $r > d$ melting temperature tends to the value characteristic of the bulk sample. Therefore, the parameter d is naturally called the thickness of the surface layer of metal.

From (2) and (4):

$$d = 2,41 \cdot 10^{-4} \cdot v \text{ (} M^{-2} \cdot \text{моль)} \quad (5)$$

According to the (5), the thickness of the surface layer is defined by a single parameter - v , i.e. the atomic structure of the metal. Equation (5) also allows you to estimate the thickness of the surface layer of metal on the known value of v . For example, for gold $v = 10,2 \text{ cm}^3/\text{mol}$ and the ratio of (5) gives $d = 2,45 \text{ nm}$.

In [5] to the surface tension of the nanocrystal obtained by the following expression:

$$\sigma(r) = \sigma_\infty \left(1 - \frac{d}{r} \right), \quad (6)$$

where $\sigma_\infty = \sigma$ - the surface tension of the bulk sample, the parameter d has the same meaning as in the previous cases.

Formula (6) in the form coincides with the formula Gibbs - Tolman - Koenig - Buff:

$$\sigma(r) = \sigma_\infty \left(1 - \frac{2\delta}{r} \right), \quad (7)$$

where δ is called the Tolman constant or Tolman length [6].

It is believed that this option can not be determined experimentally. In this case, a constant Tolman $\delta = d/2$, which can be determined experimentally. Formula (6) coincides with the mathematical formula (1).

4. Experimental results

Fig. 1 shows the size dependence of the luminescence intensity of the KCl-Tl phosphor, and Fig. 2 - size dependence of the magnetic susceptibility of magnetite.

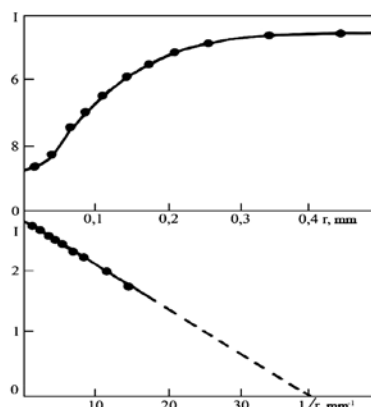


Figure 1. The dependence of KCl-Tl luminescence intensity of the phosphor grain size [7].

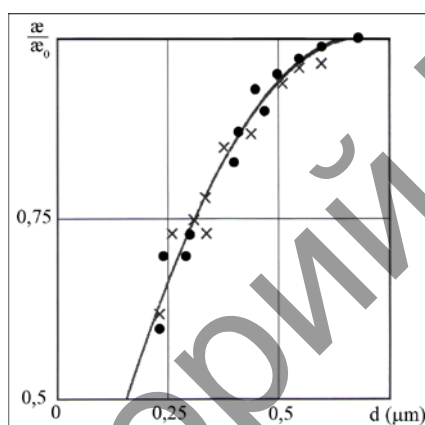


Figure 1. The dependence of the magnetic susceptibility of the diameter of the magnetite grains [8].

In both these cases, depending describe with great accuracy the formulas:

$$I = I_0 \left(1 - \frac{d}{r}\right), \quad \chi = \chi_0 \left(1 - \frac{d}{r}\right). \quad (8)$$

Here the parameter d is calculated by formula (2) and determines the corresponding surface of the material layer thickness. In the coordinates $I/I_0 \sim 1/r$ dependence in Fig. 1 and 2 give a straight tangent of the angle which is equal to d . This makes it possible to determine the surface tension of the dielectric and magnetic materials.

5. Discussion

For most metals, the melting temperature of nanoparticles of various sizes are presented in Table 1.

Table 1. The melting point of pure metal nanoparticles (M - metal)

M	T_∞, K	T_m, K $r = 1 \text{ nm}$	T_m, K $r = 10 \text{ nm}$	T_m, K $r = 50 \text{ nm}$
Li	452	188,3	396,5	440,1
Na	371	119,7	306,6	356,1
K	337	71,7	246,1	314,1
Rb	312	60,0	219,7	287,7
Cs	302	48,7	198,7	273,6
Be	1558	556,3	1320,4	1558
Mg	923	225,1	704,6	869,1

Ca	1118	139,8	657,6	980,7
Sr	1030	110,8	562,8	883,6
Ba	983	99,3	520,1	834,5
Al	933	291,6	764,8	933
Ga	302,8	159,3	277,6	297,3
In	429	165,0	369,8	415,7
Tl	576	169,4	464,5	549,6
Si	1686	285,8	1131,5	1535,9
Ge	1231	246,2	879,3	1140,0
Sn	505	168,3	420,8	485,6
Pb	600	166,7	600,0	600,0
Se	493	170,0	414,3	475,0
Te	725	161,1	537,0	676,7
Cu	1356	411,0	1102,4	1296,4
Ag	1234	301,0	942,0	1162,0
Au	1336	310,7	1004,5	1253,3
Zn	693	277,2	602,6	672,8
Cd	594	204,8	499,2	572,3
Hg	234	127,7	216,1	230,2
Cr	2173	452,7	1574,6	2019,5
Mo	2873	383,1	1741,2	2542,5
W	3673	390,7	1996,2	3144,7
Mn	1517	399,2	1185,2	1436,6
Tc	2473	405,4	1637,7	2244,1
Re	3423	422,6	2001,8	2997,4
Fe	1808	441,0	1380,2	1702,5
Co	1763	464,0	1377,3	1670,0
Ni	1726	466,5	1359,1	1637,6
Ce	1077	168,3	699,4	972,0
Pr	1208	172,6	755,0	10,78,6
Nd	1298	175,4	791,5	1150,7
Sm	1325	181,5	812,9	1176,7

From Table 1 it is seen that the melting temperature of nanoparticles with sizes of 1 nm is much lower than the melting temperature of the bulk sample. Part of the metal at such sizes are thermally unstable at room temperature.

Table 2 shows the values of d , calculated by the formula (5). From Table 2 it is seen that the thickness of the surface layer of pure metals is not more than 10 nm. This means that the surface layer is a pure metal nanostructure.

Consider the account of the size dependence of the physical properties of small particles on the example of the theory of homogeneous nucleation of a new phase.

Table 2. Surface layer thickness d pure metals

M	d, nm	M	d, nm	M	d, nm
Li	0,7	Sr	5,8	Sn	1,4
Na	1,5	Ba	6,2	Pb	1,8
K	2,6	Al	1,5	Se	1,3
Rb	2,9	Ga	0,6	Te	2,5
Cs	3,6	In	1,1	Cu	1,6
Be	1,3	Tl	1,9	Ag	2,2

Mg	2,2	Si	3,4	Au	2,4
Ca	4,9	Ge	2,8	Zn	1,1
Cd	1,3	Fe	2,2	Gd	5,3
Hg	0,6	Co	2,0	Tb	5,3
Cr	2,7	Ni	1,9	Dy	5,3
Mo	4,6	Ce	3,8	Ho	5,5
W	5,8	Pr	4,2	Er	5,5
Mn	2,0	Nd	4,5	Tm	5,2
Tc	3,6	Sm	4,4	Yb	4,6
Re	4,6	Eu	5,8	Lu	5,7

The main provisions of the theory of formation of new phase nuclei were advanced by Gibbs and then developed by Volmer, Becker and Doering, Stransky and Kaishev, Frenkel, Zeldovich et al. [9]. Despite various modifications and refinement of classical nucleation theory, and it is quite correct qualitative description of nucleation process, it is still far from matching the experimental and theoretical data.

According to the classical theory of nucleation of a new phase in the old metastable phase is considered as a fluctuation process. In the case of the crystallization of a supercooled melt critical radius of a nucleus can be expressed in terms of supercooling ΔT [9]:

$$r_k = 2M\sigma T_0 / \rho q \Delta T, \quad (9)$$

where M - molecular weight; ρ - the density of crystal-nucleus; q - heat of fusion; T_0 - temperature equilibrium of the two phases of infinitely large radius, σ - interfacial tension of crystal-nucleus.

In most studies it is considered that homogeneous nucleation of metal crystals begins with the supercooling $\Delta T = 0.2T_m$ of the melting temperature. Assuming that $T_0 = T_m$, we obtain:

$$r_k = 10M\sigma / \rho q. \quad (10)$$

All values in the expression (11) (except σ) are determined experimentally with great precision and are listed in directories. For pure metals surface tension value σ_0 is defined in [4]. The interfacial surface tension at the crystal - melt is approximately equal to: $\sigma \approx 1/3\sigma_0$. Then the calculation of the classical formula (11) gives a value for the critical radius of the order of a micron or a fraction of that in the three orders of magnitude the experimentally observed values.

In [10] takes into account the size dependence of all the quantities in the equation (11) and calculated the critical radius of nucleation of solid phase of pure metals (Table 3).

Table 3. Critical radius of homogeneous formation of the pure metals [10]

M	rk, nm	M	rk, nm	M	rk, nm	M	rk, nm
Li	0,5	Sr	2,8	Sn	0,7	Cd	0,6
Na	0,7	Ba	2,9	Pb	0,8	Hg	0,3
K	1,2	Al	0,7	Se	0,6	Cr	1,3
Rb	1,4	Ga	0,3	Te	1,2	Mo	2,2
Cs	1,7	In	0,5	Cu	0,8	W	2,8
Be	0,6	Tl	0,8	Ag	1,0	Mn	0,9
Mg	1,0	Si	1,6	Au	1,1	Fe	1,0
Ca	2,3	Ge	1,3	Zn	0,5	Co	0,9

Table 4 shows the experimental values of the critical range from [11].

Table 4. Critical radius of homogeneous formation of the pure metals [11]

M	rk, nm	M	rk, nm
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Ga	0,9	Ge	0,9
Sn	1,2	Ag	1,2
Cu	1,1	Pb	1,1
Bi	0,8	Hg	0,8

Compare values from Tables III and IV show good agreement, which speaks in favor of the developed approach.

From the above discussion, it follows that in the classical theory does not take into account the size dependence of the surface tension, the melting point and other physical properties of small particles. Therefore, the discrepancy between theory and experiment is so impressive, despite the fact that the approach is based on fluctuations of no objection to the theory.

6. Conclusion

From the above it follows universal dependence of physical properties of A (r) nanomaterial on its size:

$$A(r) = A_{\infty} \left(1 - \frac{d}{r} \right). \quad (11)$$

Discovered universal relationships enable us to calculate the physical properties (mechanical, electrical, magnetic, thermal, etc.) of small particles and thin films based on knowledge of the properties of bulk materials.

The work was supported by a grant from the RSF № 17-19-01224.

References

- [1] Kreibig U, Vollmer M 1995 *Optical Properties of Metal Clusters*. Berlin, Heidelberg: Springer Verlag 532.
- [2] Makarov G.N. 2010 *Advances of Physical Sciences* **180** (2) 185–207
- [3] Buffat Ph, Borel J P 1976 *Phys. Rev. A* **13** (6) 2287–2298
- [4] Yurov V M 2012 *Bulletin of the University. Physics* **3** (67) 27–35
- [5] Yurov V M, Ibraev N H, Guchenko S A 2011 *Russian Physics Journal* **54/3** 335–340
- [6] Rekhviashvili S S, Kishitkova E V, Karmokova R Y et al. 2007 *Technical Physics Letters* **33** (2) 1–7
- [7] Aluker E D, Lucys D M, Chernov S A 1979 *Electronic excitation and radioluminescence alkali halide crystals Riga: Zinatne* 251.
- [8] Yurov V M 2009 *Modern problems of science and education* **4** 152–156
- [9] Danilov A I, Polukarov Y M 1987 *Russian Chemical Reviews* **56** (7) 1082–1104
- [10] Yurov V M 2015 *Physico-chemical aspects of the study of clusters, nanostructures and nanomaterials* **7** 548–554
- [11] Skripov V P, Kaverda V P 1987 *Problems of modern crystallography* 232–246