UDC 538.97; 539.216.2; 539.23

SURFACE ENERGY AND THE TOLMAN CONSTANT OF HALOGENIDE OF ALKALI METALS

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The article reviews the existing methods for determining the surface energy of solids. Each of the methods described is practically limited to either temperature or values that are experimentally determined with low accuracy. A method is proposed for determining the surface energy of a solid on the basis of the dimensional dependence of its physical properties (magnetic permeability, luminescence intensity, thermal conductivity, etc.). The surface energy of alkaline halides is determined. Its magnitude is much larger than the surface energy of pure metals. The critical radius of these compounds is calculated, starting with which the direct Hall-Petch effect is reversed.

Keywords: surface energy, size effect, luminescence, halides, alkali metals.

Introduction

Methods for determining the surface energy of solids began to be developed in the 20s of the last century [1, 2]. In the sixties of the last century, some results of research were presented [3, 4]. The following methods for determining the surface energy of solids were proposed [3, 4]:

1. The method of "zero creep".
2. Method of destruction (splitting) of crystals.
3. The "neutral drop" method.
4. Method of dissolving the powder
5. The method of stages of growth and evaporation.
6. The method of a conical sample.
7. Method of "healing scratch".

The idea of the "zero creep" method is as follows. At a high temperature under the influence of surface tension forces, the arbitrary shape of a solid body must be transformed in the direction of decreasing the total surface energy. Thus, in particular, a freely suspended sample of a thin wire or foil should be shortened in length. On the other hand, under the influence of externally applied force (F), the foil (or filament) can be elongated due to the viscous flow. Obviously, for a certain value of F = F *, the surface tension forces will be compensated and the creep rate will vanish. An experimentally determined F * can be a source of information on the magnitude of the surface tension. This method was used to determine the surface energy of pure metals at a temperature close to the melting point, when the mobility of the atoms becomes noticeable. For other materials, this method does not apply.

The most reliable version of the method of determination, based on cleavage of the crystal, was proposed in 1930 Obreimov [2]. The idea of this work is as follows. From the crystal along the cleavage plane, plastic is split off, which under the influence of the moment of forces acting against the forces of surface tension, partially bends. This plate can be used as a dynamometer measuring the splitting force. The method was applied in [3] (Gilman J.) for various crystals at a temperature of liquid nitrogen, when the heat arising from the splitting of the crystals can be neglected. The method is suitable for crystals having a cleavage plane.

The value of σ_s can be determined from the data on the equilibrium form of the liquid droplet of another substance (B), which is located on the surface of the solid (A) under study. The measurement scheme is clear from Fig. 1.

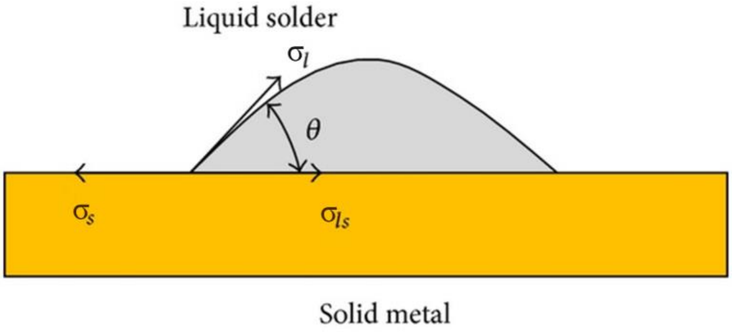


Fig.1. Diagram of the "neutral drop"

In the method for dissolving the powder, the value is found from the calorimetric determination of the dissolution heat difference of the dispersed powder and a massive crystal of the same mass ($\sigma_s = q_r - q_0/S$). The source of the significant error in the method described is the inaccuracy in the determination of the total surface of the powders. The generally accepted assumptions that the shape of the powder are spherical and all the powders are the same can lead to large errors.

To determine the amount of surface energy in the method of growth and evaporation stages, one uses the fact that on the growth surface there are often observed retarded "resting" steps whose curvature is such that the equilibrium vapor pressure near the step surface coincides with the vapor pressure in the space surrounding the crystal. The accuracy of the method is small.

Directly in the method of a conical sample, not the surface energy but the quantity (interfacial surface tension at the liquid-solid interface) is determined at the melting temperature [4]. The method is rarely used. It is known that in the case of high-temperature annealing of a crystal under equilibrium conditions, on the surface of which a scratch is applied, the latter is smoothed out. For metals, the kinetics of smoothing is determined by the mechanism of surface diffusion. This is the basis of the method of "healing scratch" [4].

As follows from the review [1-4] of experimental methods for determining the surface energy of solids, each of the methods described is practically limited to either temperature or values that are experimentally determined with low accuracy.

At present, various modifications of the "neutral drop" method have become most widespread. This method is based on Young's equation [5], which leads to the concept of the contact angle θ (Fig. 1). There are two models for describing the contact angle on a real surface. The Wenzel model and the Cassie-Baxter model. Unlike an ideal surface, a real surface can have a chemical heterogeneity and surface roughness. The Wenzel model considers a rough surface, but with chemical homogeneity [6]. The Cassie-Baxter model considers a plane surface, but with a chemical inhomogeneity [7]. These models have been widely used to the present time. However, today they have been seriously criticized [8]. More complex models of the contact angle have been developed [9-13].

In [13], the Young equation, the Wenzel equation, and the Cassie-Baxter equation were obtained from the thermodynamic point of view. From the conclusions, the behavior of the contact angle could be determined. In an ideal situation, the contact angle is determined by an infinitesimally small region near the contact line, and not by the inner surface inside the contact line. The angle of contact also does not depend on external factors that do not affect the surface energy. Thus, it is not influenced by pressure, droplet size, gravity, curvature of the substrate surface, rotation of the substrate and the presence of needles or defects. From the point of view of the hysteresis of the contact angle, it was explained why these equations are not correct for describing real common surfaces, although the Cassie-Baxter equation is widely used for a superhydrophobic surface. In addition, the limitations of the equations were discussed. It is expected that this study will provide a deeper understanding of the correctness of the models of contact angles and the nature of the contact angle.

1. Experimental method

The foundations of the thermodynamics of curvilinear interfaces were laid by J. Gibbs [14]. Then R. Tolman and his followers reduced this problem to the account of the dimensional dependence of the surface tension. In 1949, R. Tolman derived the equation for the surface tension σ [15]

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

Here σ_∞ is the surface tension for a plane surface; Rs is the radius of the tension surface; $\delta > 0$ is the distance between an equimolecular separating surface and a tension surface for a plane boundary. The order of magnitude of the parameter δ, called the Tolman length or the Tolman constant, should be comparable to the effective molecular diameter a. For $R >> \delta$ Tolman's formula can be rewritten in the form:

$$\sigma/\sigma_\infty = 1 - 2\delta/R, \qquad (2)$$

Subsequent studies did not change the content and form of the equation (2).

On the basis of quantum statistical thermodynamics we obtained the response function of the system W to the external action in the form [16]:

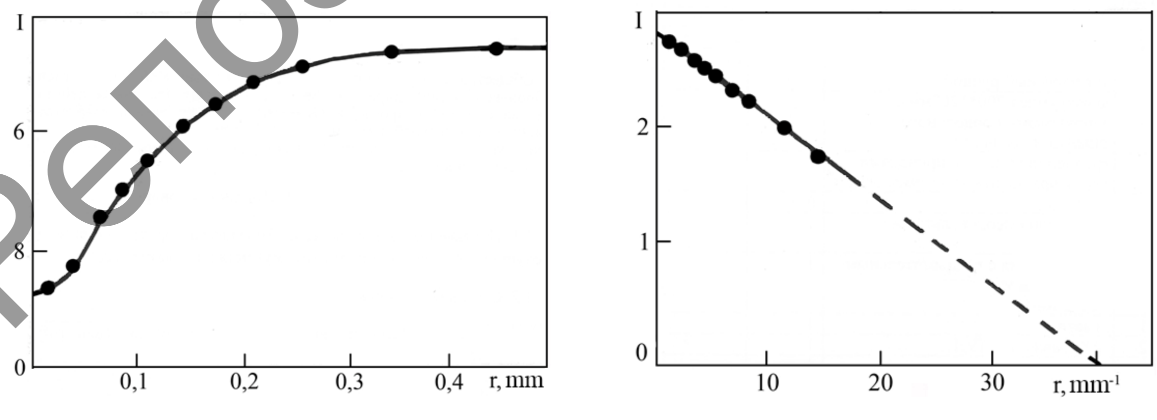
$$W/W_\infty = 1 - d/R \qquad (3)$$

The parameter d is related to the surface tension σ by the formula:

$$d = \frac{2\sigma\upsilon}{RT} \qquad (4)$$

Here σ is the surface tension of a massive sample; υ is the volume of one mole; R is the gas constant; T-temperature.

Equations (3) and (4) were used by us to develop a method for determining the surface tension of solids [17]. The method was used to determine the surface tension of dielectric crystals KCl, with an admixture of thallium ions as a luminescent probe (W=I). The intensity of X-ray luminescence I was determined by the standard photoelectric method. The grain size of the dielectric was determined using a metallographic microscope. The results are shown in Fig. 2.



a b

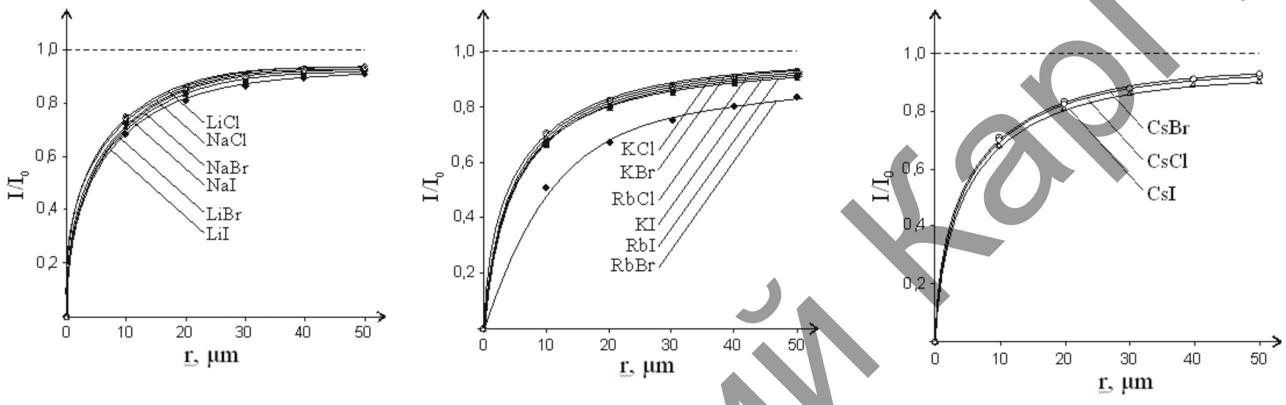
Fig. 2. Dependence of the intensity of X-ray luminescence KCl (a) on the size of the phosphor grain (b):

In the coordinates $I \sim 1/r$, the experimental curve is rectified in accordance with (3), giving a value of d = 0.02 μm. For KCl υ= 74.6 cm^3/mol and from (4) for surface tension, we obtained: σ=0.730 J/m^2.

Note that as a function of the W response in equation (3), most physical properties that depend on the particle size or the film thickness (magnetic susceptibility, dielectric constant, thermal conductivity, etc. (can be used and determine the surface tension of a rigid body).

2. Results of the experiment and their discussion

The experimental results are shown in Fig. 3 and in Table 1.



a b c

Fig.4. Surface tension of halogenide of alkali metals: a – Li, Na; b – R, Rb; c - Cs

Table 1. Surface tension and constant Tolman of alkali metal halides

Metal	T_m, K	σ_m, J/m^2	d, nm	υ, g/mol	δ, nm
LiCl	878	0.615	20.9	42.4	10.5
LiBr	825	0.578	40.1	86.8	20.1
LiI	742	0.519	55.5	133.6	27.8
NaCl	1074	0.752	35.1	58.4	17.6
NaBr	1020	0.714	58.8	102.9	29.4
NaI	934	0.654	78.4	149.9	39.2
KCl	1043	0.730	43.6	74.6	21.8
KBr	1007	0.705	67.1	119.0	33.6
KI	954	0.668	88.7	166.0	44.4
RbCl	991	0.694	67.1	120.9	33.6
RbBr	954	0.668	88.4	165.4	44.2
RbI	920	0.644	109.4	212.4	54.7
CsCl	918	0.643	86.6	168.4	43.3
CsBr	909	0.636	108.3	212.8	54.2
CsI	894	0.626	130.1	259.8	65.1

For h <d, formula (3) loses its physical meaning (A (h) → ∞), so we extend the function A (h) in this region so that the function A (h) vanishes at the point h = 0. This condition is satisfied when the function (3) is rewritten as:

$$A(r) = A_0 \cdot \left(1 - \frac{d}{d+h}\right) \tag{5}$$

The parameter d is naturally interpreted as the thickness of the surface layer (Fig. 4)

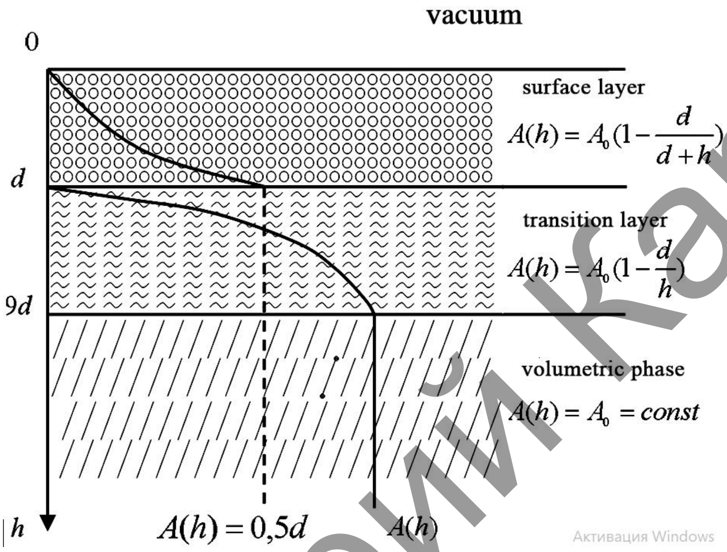


Fig.4. Schematic representation of the surface layer

Let us compare the parameter d for alkali metal halides with pure metals (Table 2).

Table 2. Parameter d of pure metals (M)

M	d, nm	M	d, nm	M	d, nm	M	d, nm	M	d, nm	M	d, nm
Li	1.4	Sr	8.3	Sn	2.0	Cd	1.9	Fe	3.1	Gd	7.6
Na	2.1	Ba	8.9	Pb	2.6	Hg	0.8	Co	2.8	Tb	7.5
K	3.7	Al	2.2	Se	1.9	Cr	3.8	Ni	2.7	Dy	7.6
Rb	4.2	Ga	0.9	Te	3.5	Mo	6.5	Ce	5.4	Ho	7.8
Cs	5.2	In	1.6	Cu	2.3	W	8.4	Pr	6.0	Er	7.8
Be	1.8	Tl	2.4	Ag	3.1	Mn	2.8	Nd	6.4	Tm	7.4
Mg	3.1	Si	4.9	Au	3.3	Tc	5.1	Sm	6.3	Yb	6.5
Ca	7.0	Ge	4.0	Zn	1.5	Re	7.1	Eu	8.3	Lu	8.2

From Table 2 it is seen that the thickness of the surface layer of pure metals does not exceed 10 nm. This means that the surface layer of pure metal is a nanostructure. For halides of alkali metals, the thickness of the surface layer varies from 80 to 250 nm. This means that dimensional effects are observed even at R ~ 10d ~ 2000 nm. It should be noted that the Tolman constant δ = d/2 has no physical meaning as the thickness of the monomolecular layer.

Experimental studies of the mechanical properties of nanomaterials and nanostructured coatings have shown that the tensile strength and hardness of many metals (Pd, Cu, Ag, Ni, etc.) are significantly higher than in the corresponding massive analogues. The increase in hardness and strength with decreasing grain size to a certain critical size is practically characteristic for all crystals. This follows from the well-known Hall-Petch equation that the yield stress σT depends inversely on the average grain size d [18, 19]:

$$\sigma_T = \sigma_M + kd^{-1/2}, \tag{6}$$

where σ_M is the ultimate strength of a single crystal, k is a certain dimensional coefficient.

Typically, the Hall-Petch relation (5) is satisfied for a significant part of the nanomaterials studied only up to a certain grain size, and at its lower values, reverse effects are observed: hardness (strength) decreases as the grain size decreases.

Despite the large number of works on the study of the influence of the size factor on the mechanical properties of nanostructures, the physical mechanisms of this influence remain the subject of ongoing discussions [20-25]. In [26] for the yield point we obtained the equation:

$$\sigma_T = \sigma_M + C\sigma d^{-1/2}. \tag{7}$$

Equation (7) coincides in form with the Hall-Petch equation (6). However, the proportionality coefficients in these formulas differ. In the case of equation (7), the behavior of the yield stress of small particles is also determined by the value of their surface tension σ.

For small d, A.I. Rusanov obtained an asymptotic linear dependence [27]:

$$\sigma = Kd. \tag{8}$$

Here K is the coefficient of proportionality. Formula (8) was obtained on the basis of thermodynamic considerations and should be applicable to small objects of a different nature. In this case, equation (7) takes the form:

$$\sigma_T = \sigma_M + CKd^{1/2}. \tag{9}$$

Equation (9) is the inverse Hall-Petch effect. It follows from equation (7) that the Hall-Petch equation begins to break from the moment when the dimensional dependence of the surface tension (R<d) begins to appear.

From Table 1 it can be seen that the strength of alkali metal halides is replaced by ductility at rather large d values. This affects many properties of these crystals.

Conclusion

The proposed method for determining the surface energy of a solid body with respect to the dimensional dependence of its physical property allows one to make a comparison with several methods. The implementation of each method does not cause any difficulties. This is illustrated by the calculation of the surface energy of alkali metal halides.

ACKNOWLEDGEMENTS

The work was carried out under the program of the Ministry of Education and Science of the Republic of Kazakhstan Grants No. 0118RK000063 and No. Ф. 0780.

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Article accepted for publication 14.05.2018