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Effect of an electric field on nucleation and growth of crystals

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Effect of an electric field on nucleation and growth of crystals

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Abstract. The effect of the electric field strength on nucleation and growth of the crystals of ammonium halides and alkali metal sulfates has been studied. The optimal electric field strength for NH_4Cl and NH_4Br crystals was found to be 15 kV/cm, and for NH_4I, it equaled 10 kV/cm. No effect of the electric field strength on the crystal growth was found for alkali metal sulfates. This difference is analyzed in terms of the crystal growth thermodynamics. In case, when the electric field is small and the Gibbs energy is of a significant value, the influence of the electric field at the crystal growth is negligible. A method to estimate the critical radius of homogeneous nucleation of the crystal is suggested.

1. Introduction

The effect of electric, magnetic and other fields on nucleation and growth of various crystals has been studied since 50-ies of the last century. Some qualitative patterns were found and empirical models were suggested. However, the quantitative theory of these effects has not been worked out. This is primarily due to the lack of a rigorous theory of homogeneous nucleation. The main ideas of the theory of new phase nucleation were put forward by Gibbs and then developed by Volmer, Becker and Doring, Stransky and Kaishev, Frenkel and Zeldovich. According to this theory, the formation of small particles of a new phase in the metastable phase is considered as a fluctuation process. Despite this progress, there is no quantitative agreement between the theory and experimental data.

This is due to the fact that the size effects in the formation of crystal nuclei which have dimensions of the order of (1–5) nm are ignored. If we consider the size dependence of the surface tension at the interface only, classical theories of crystallization nucleation provide satisfactory quantitative agreement between theoretical and experimental data [1]. In [2], an additional force generated when applying the electric field was introduced. The results obtained in this research show that an electric field can either stimulate or inhibit the nucleation process depending on the ratio of the dielectric constant and orientation of the applied electric field relative to the surface nucleation. This approach is demonstrated in [3], which provides extensive bibliography on the effect of the electric field on crystal nucleation and growth. This issue is addressed in the reviews in [4–6].

2. Effect of the electric field on nucleation and growth of crystals of ammonium halides

A V Shubnikov [7] observed nucleation under the action of the electric field in the ammonium chloride solution. He attributed the observed phenomenon to the presence of the smallest dust particles in air which enter the solution and become the crystallization sites under the action of the electric field.

In [8], Kozlowsky experimentally investigated the effect of the electric field on the solution of halides and sulfates. The field strength was varied from 1 to 30 kV/cm. The experiments showed that the electric field does not affect the sulphate solutions of nickel and copper and weakly impacts the nucleation process in the cadmium iodide solution. However, a significant impact of the field was observed on solutions of sodium and potassium chloride and NH_4I.

We have conducted a detail study of the effect of the electric field on nucleation and growth of ammonium halide crystals. Note that in [7, 8], as in many other studies, ammonium halides were produced in the form of dendrites. Nobody succeeded to produce single crystals of ammonium halides.

A small amount of urea was added to 90 % aqueous solution of ,   and . The temperature in the thermostat was maintained at 35 ° C. When the intensity of the electric field increased from 0 to 3 kV/cm, the number of centers increased as well. In the range from 3 to 15 kV/cm, the number of nuclei decreased, however, larger and more transparent crystals emerged. The optimal electric field strength for and was equal to 15kV/cm, and for it was 10 kV/cm.

3. Theoretical aspects of the effect of the electric field on crystal nucleation and growth

Thermodynamic methods used in [8] showed under the impact of the electric field, the crystallization pressure changes

$$P - P_0 = \frac{\beta E^2}{V_1 - V_2} \tag{1}$$

where $\beta = \text{const}, V_1, V_2$ are the specific volumes of the first and second phases (per molecule), respectively.

The critical radius of the nucleus in the solid phase in the electric field:

$$r^* = \frac{2\sigma V_2}{\Delta\mu^0 - \beta E^2} \tag{2}$$

where σ is the coefficient of the surface tension at the solution-crystal interface; $\Delta\mu^0$ is the chemical potential in the absence of the field.

For a one-component composition , where ΔG is the Gibbs energy. According to [1] the N value is of the order of 100. Table 1 shows the values of the Gibbs energy (in modulus) for some of the substances taken from [9].

Table 1. Gibbs energy for some halides and sulfates [9]

Substance/Agent	ΔG (kJ/mol)	Substance/Agent	ΔG (kJ/mol)
KCl	408.490	$CuSO_4$	661.070
NaCl	384.120	$CuSO_4 \cdot 5H_2O$	1377.780
NH_4Cl	202.770	$NiSO_4 \cdot 6H_2O$	2680.050
AgCl	109.700	$NiSO_4 \cdot 7H_2O$	2459.640
AgBr	97.250	K_2SO_4	1318.790

Taking into account the remarks above equation (2) will take the form:

$$r_{\text{к}} = \frac{2\sigma\vartheta_2}{G/N-\beta E^2} \tag{3}$$

In case, when the electric field strength is low and the Gibbs energy is of a significant value, i.e. $G/N >> \beta E^2$, the effect of the electric field on the crystal growth will be negligible. As can be seen in Table 1, the sulfate solution having a larger value of the Gibbs energy will be less affected by the electric field. This is consistent with the results reported in [2, 8].

4. Evaluation of the critical radius of homogeneous nucleation of crystallization sites

The evaluation of the critical radius of homogeneous nucleation of pure metals can be carried out in the parameter d, which is determined by the size dependence of some physical property A (r) of metal (magnetic, electric, etc.) according to the formula [1]:

$$A(r) = A_0\left(1-\frac{d}{r}\right), \tag{4}$$

where A_0 is the physical property of the bulk sample.

Equation (4) is valid for both internal and external size effects. Therefore, the developed approach is valid not only for crystallization of pure metals, but for any other material. In this case, the parameter d can be determined by one of the proposed methods [10], and the formula $r = r_c \geq d/3$ can be used to evaluate r_c.

We defined the parameter d of the intensity I (r) of the luminescence of crystalline powders of size. The parameter $d = 2\sigma\upsilon / RT$, where σ - the surface tension of the crystal, υ - molar volume, R - the gas constant, T - temperature. The coordinates I (r) ~ 1 / r a straight line is obtained according to formula (4). The slope of this straight line gives the value of d.

Table 2. Surface tension and critical radius of the alkali metal halides.

Chemical formula	Surface tension σ (J / m^2)	The critical radius r_k (nm)
NaCl	0.158	1.095
NaBr	0.138	1.181
NaI	0.118	1.283
KCl	0.141	1.414
KBr	0.123	1.420
KI	0.113	1.597
RbCl	0.130	1.497
RbBr	0.114	1.502
RbI	0.104	1.654

Tables 2 and 3 show values of the surface tension and the critical radius halides and sulfates of alkali metals. From these tables it follows that the critical radius at sulfates of alkali metals slightly larger than alkali metal halides. However, the difference in the critical radius is not as great as one would expect. This means that the electric field does not act on the nucleation process, and on their growth in accordance with the formula (3).

Table 3. Surface tension and critical radius sulphates of alkali and alkaline earth metals.

Chemical formula	Surface tension σ (J / m^2)	The critical radius r_k (nm)
Li_2SO_4	0.141	1.862
Na_2SO_4	0.124	1.753
K_2SO_4	0.117	2.044
Rb_2SO_4	0.112	2.209
Cs_2SO_4	0.110	2.504
$BeSO_4$	0.240	2.690
$MgSO_4$	0.166	2.003
$CaSO_4$	0.189	2.958
$SrSO_4$	0.180	2.226
$BaSO_4$	0.175	2.421

5. A simple model

Here we want to show a simple model, which gives some idea of the physical process of homogeneous nucleation of a new phase. In a homogeneous medium with the particle number density n probability W(r) is the first that the nearest neighbor is at a distance r_k from the selected particles, is easily obtained from the classical statistical physics, and it is equal to:

$$W(r_к) = 4\pi n r_к^2 \exp\left[-4\pi n^2 r_к^3/3\right] \tag{5}$$

The probability of finding N particles in the embryo radius r_k is obviously $W_N(r_k) = \prod_{i=1}^{N} W_i(r_k)$. The probability (5), we define the other hand, as the ratio of energy Bohr atom $\left(E = z^2/2a,\ z - \text{ch arg e},\ a = \text{const}\right)$ to the total energy (ideal gas) $\left(3/2nkT_0\right)$. This is done, something to qualitatively assess whether the different critical radius r_k of the embryo, for example, for different metals. Thus, we have:

$$\frac{z^2/2a \cdot N}{3/2nkT_0} = (4\pi n)^N r_к^N \exp\left[-4\pi N n^2 r_к^3/3\right] \tag{6}$$

Taking the logarithm of both sides of (6), and performing simple transformations, we obtain:

$$-9\ln 10+\ln\left(\lambda\frac{Z^2}{T_0}\right)+\frac{3}{2}n\frac{T_0}{\Delta T}=\frac{4\pi}{3}Nn^2r_{\kappa}^3 \tag{7}$$

The first term arises by substituting constants $\alpha = 1$ - provides a single dimension of values, T_0 - melting point, $\Delta T = T_0 - T_1$ - hypothermia. From (7) we see that the first two terms on the left are negligible compared to the rest. This immediately removes the dependence of r_k on Z, i.e, the type of atoms crystallizing substance. Finally, from (7) we have:

$$N \cdot r_{\kappa}^3 = \frac{1}{\pi n}\cdot\frac{T_0}{\Delta T} \tag{8}$$

If you make an estimate of the average values: r_k ~ 1 nm, T_0 about 1000 (for me-metals), ΔT ~ 100, n = N_L - number Loschmidt ~ 3 10^{19} cm^{-3}, we obtain for the number of particles in the bud N ~ 100. Below we provide data taken from [11]. We see that our estimates of the formula (8) in qualitative agreement with the experimental data. Indeed, the radius of the embryo practical ski does not depend on the type of metal atoms, the average number of particles N in the embryo has the same order.

Table 4. The parameters of nucleation kinetics at crystallization of supercooled metal [11].

Metal	T_0 (K)	ΔT (K)	r_k (nm)	N
Hg	234	90	0,8	100
Sn	505	180	0,8	130
Bi	544	200	0,8	30
Pb	600	170	1,1	180
Ge	1210	295	0,9	130
Ag	1234	253	1,2	430

From (8) it follows that the right side are the parameters, the magnitude of which has not changed over a wide range, i.e.:

$$N \cdot r_{\kappa}^3 \approx \text{const} \tag{9}$$

Relation (9) is approximately true for many substances. The deep causes of these correlations are not yet clear.

5. Conclusion

From the above analysis it follows that the crystal growth in the electric field does not always lead to positive results. Thermodynamic characteristics are to be considered, and it is primarily the magnitude of the Gibbs energy.

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