

## NUCLEATION AND GROWTH IN NANOMETRIC VOLUMES.

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**Abstract.** The competitive nucleation and growth of two intermediate phases in volumes of nanometric size is investigated taking into account the mole fraction depletion of the parent phase. The problem has been solved in the frame of classic method by representation of the thermodynamic potential in the mole fraction-size space. It is shown that, depending on the particle size and thermodynamic parameters of parent and intermediate phases, there exist the following possible situations: (1) total prohibition of separation, (2) formation and total stabilization of metastable phase instead of stable one, (3) relative stabilization of metastable phase with the temporary delay of its transformation into the stable phase, (4) formation and growth of stable phase, when the metastable phase does not appear at all, (5) formation and growth of stable phase via the metastable phase. Application is done to the precipitation of coherent precipitates of metastable Al<sub>3</sub>Li ordered phase in supersaturated solid solution AlLi.

### I. Introduction

Simultaneous and fast nucleation in highly imperfect supersaturated solid solutions yields very small supply regions capable to feed new phase embryos at each nucleation and growth site. As an example, the so called bulk metallic glasses (BMG) [1,2] often devitrify with a very high nucleation rate yielding, in a first crystallization stage, to a dispersion of nanocrystals in the amorphous matrix [3]. Arguing that such a high frequency of nucleation cannot be due to heterogeneous nucleation, Kelton [4] has explained such a phenomenon from an enrichment with the crystallizing component in a shell, (of atomic size width), surrounding embryos. During quenching, those frozen subcritical embryos, with their surrounding enriched shell serving as a feeding material, become overcritical and practically stops growing after

In the two dimensional approach of nucleation proposed first by Russel [6] and revisited by Kelton in the application to BMG, the enriched shell is implicitly considered as surrounded by a uniform parent phase. This means that the composition of the parent phase remains unchanged during nucleation. Application of Russel's and Kelton's theoretical approaches of nucleation are distinguishable in the sense that the first one refers to a sole nucleation event while the second is applied to simultaneous multiple nucleation events.

If one considers the simple case where the embryo contains a single component, say A, it is obvious that the number of A atoms  $N(\tau)$  in region of radius R must be much greater than the number of A atoms in the critical nucleus. Taking account of the expression of  $R(\tau)$ , and evaluating the nucleation time from the Russel approach [6] it can be established, after some algebra, that this condition is satisfied when:

Here  $\sigma$  is the parent phase-cluster interface energy,  $a$  is the interatomic distance,  $X_0$  is the mole fraction of A in the undisturbed parent phase,  $v$  is the volume per atom in the parent phase,  $v_1$  is the volume per atom of the cluster. Taking  $a = 0.3 \cdot 10^{-9} m$ ,  $X_1 = 0.5$ ,  $X_0 = 0.05$ ,  $v \approx v_1$  and  $T = 600 K$  the previous condition is satisfied only when  $\sigma \ll 0.2 Jm^{-2}$ ; condition which appears to be somewhat restrictive particularly when incoherent precipitation occurs.

Furthermore, when simultaneous multiple nucleation at the nanometer scale is developing, each nucleation event is confined in a supply region of radius  $R$  from which the embryo can be fed up to its critical size. The amount of  $A$  atoms in this region must be significantly larger than the number of atoms  $N^*$  in the critical nucleus. Otherwise the region would be too much depleted giving an important increase of the barrier of nucleation able to suppress the transformation. The

$r^*$  is the critical radius of nuclei. Taking  $r^* = 10^{-9} m$ ,  $X_0 = 0.2$  and  $v/v_1 \approx 1$ ,  $X_1 = 0.7$





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First, the thermodynamics associated with the formation of a single intermediate phase in a nanometric volume is treated.

## II. Nucleation and Growth of Single Intermediate Phase in a Small Volume

As this work is based on a thermodynamic approach, it can be considered that at any moment and at any size  $r$  (radius) of growing nucleus, mole fraction distribution is supposed to be steplike (without transient layers) so that concentration is uniform inside each phase. Analogous scheme, for single intermediate phase, has been proposed [7] in the frame of Cahn-Hilliard approach [8] with gradient terms and diffuse interface.

It is suggested that for any given nucleus size  $r$ , the mole fractions  $X_{new}$  and  $X_0 + \Delta X$  in the new and parent phases respectively satisfy the condition of minimum for the Gibbs free energy. The mole fractions are related by the following conservation law:

$$X_o \cdot V_o = X_{new} \cdot V_n + (X_o + \Delta X) V_\alpha. \quad (1)$$

In relation 1, the number of atoms per unit volume  $n$  is taken the same for old and new phase. For spherically symmetric clusters the volume of phases are such:

$$V_n = \frac{4}{3} \pi r^3, V_\alpha = \frac{4}{3} \pi (R^3 - r^3), V_o = \frac{4}{3} \pi R^3.$$

Thus, mole fraction  $X_{new} = X_{new}(\Delta X)$  is a function of depletion  $\Delta X$ . Solving the variation problem  $\frac{\partial \Delta G}{\partial \Delta X} = 0$  an optimal depletion for fixed nucleus size is obtained provided by the condition  $\frac{\partial^2 \Delta G}{\partial \Delta X^2} > 0$ .

The driving force for transformation for the entire system is:

$$\Delta G_{tot} = N_{ct} \Delta G. \quad (2)$$

$N_{ct}$  is the number of nucleation sites in the system,  $\Delta G$  is the driving force of transformation per one nucleation site which can be expressed:

$$\Delta G = n \cdot (V_n \cdot \Delta g_{new}(X_{new}) + (V_o - V_n) \cdot \Delta g_{old}(X_o + \Delta X) - V_o \cdot \Delta g_{old}(X_o)) + \sigma \cdot S. \quad (3)$$

$X_{new}$  is related to  $X_o$  by the following equation:  $X_{new} = X_o + \left(\frac{R^3}{r^3} - 1\right)(-\Delta X)$ ;  $\sigma$  and  $S$  are the interface energy and the interface area formed between the two phases respectively;  $\Delta g_{new}(X_{new})$ ,  $\Delta g_{old}(X_o + \Delta X)$ ,  $\Delta g_{old}(X_o)$  are the Gibbs energies of formation (per atom) at a given temperature.

One can easily check that the condition  $\left(\frac{\partial \Delta G}{\partial \Delta X}\right)_{r,R} = 0$  coincides with the classical parallel tangents rule but here when depletion of the parent phase is taken into account. This is represented in figure 2.

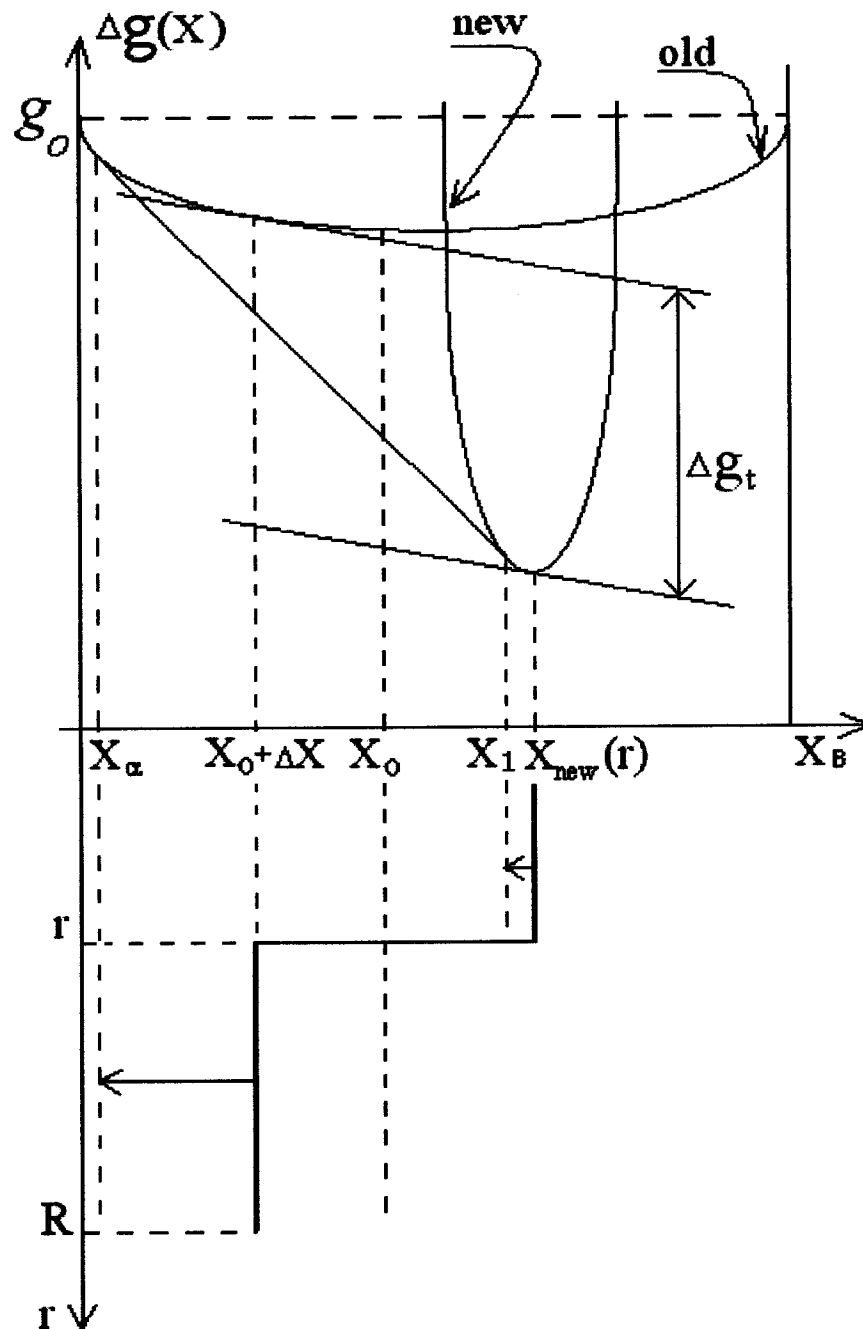


Fig. 2 Dependencies of Gibbs energy (per atom) on composition and mole fraction profile for nucleus precipitating in the limited volume. Mole fractions  $X_{new}$  and  $X_0 + \Delta X$  are linked by the parallel tangents rule, they depend on the nucleus radius  $r$  and provide the minimization of  $\Delta G$  for every given  $r$ ,  $R$ . For the case of full decomposition in the system these mole fractions  $X_{new}$ ,  $X_0 + \Delta X$  tend to the values  $X_1$ ,  $X_\alpha$  determined by the common tangent rule corresponding to equilibrium.  $\Delta g_t$  is the driving force of transformation per one atom of the nucleus,  $g_o$  is the reference level.

Using a parabolic representation for the Gibbs energy of formation as a function of concentration [7,9] it follows (figure 2):

$$\Delta g_{new}(X) = \Delta g_{new}(X_n^0) + \frac{\alpha_{new}}{2} (X - X_n^0)^2, \quad (4)$$

$$\Delta g_{old}(X) = \Delta g_{old}(X_o^0) + \frac{\alpha_{old}}{2} (X - X_o^0)^2. \quad (5)$$

After some algebra, the expressions obtained for the optimal concentration depletion and the optimal concentration of the new phase are the following:

$$\Delta X^{opt} = - \frac{X_n^0 + \frac{\alpha_{old}}{\alpha_{new}} (X_o^0 - X_o^0) - X_o^0}{\frac{R^3}{r^3} - 1 + \frac{\alpha_{old}}{\alpha_{new}}}; \quad X_{new}^{opt} = \left( \frac{R^3}{r^3} - 1 \right) (-\Delta X^{opt}) + X_o^0. \quad (6)$$

Substituting  $\Delta X^{opt}(r, R)$  and  $X_{new}^{opt}(r, R)$  into expression for  $\Delta G$ , one obtains  $\Delta G$  as a function of one "reaction coordinate"  $r$  (at fixed  $R$ ). Hereby the optimal mole fraction in the parent phase will be  $X_o + \Delta X^{opt}(r, R)$ .

Choosing the following values for the parameters:  $n = 6 \cdot 10^{28} m^{-3}$ ,  $X_o = 0.32$ ,  $X_n^0 = 0.8$ ,  $X_o^0 = 0.2$ ,  $\Delta g(X_n^0) - \Delta g(X_o^0) = 0$ ,  $\alpha_{new} = \alpha_{old} = 10^{-19} J$  and  $\sigma = 0.15 Jm^{-2}$ ,  $\Delta G(r, R)$  has been calculated and represented in figure 3.





For  $R = 2.8nm$  (situation II in figure 3) a function  $\Delta G(r)$  has a metastable minimum laying for higher Gibbs energy than the initial state.

For large  $R$  ( $R = 3.2nm$ , situation I in figure 3)  $\Delta G(r)$  presents the classical form with one maximum defining the nucleation barrier  $\Delta G(r^*)$  and a minimum corresponding to final decomposition.

Situations I and II, in the case of multiple simultaneous nucleation at nucleation sites can be compared to the so called «mob effect»: "If people pass the door one by one, they all do succeed, but if they try to do it simultaneously, the process stops".

Of course, such a situation at the entire sample scale remains metastable from a kinetic point of view. For example, if a system has got into metastable minimum, some of the nuclei will turn back, and others will grow using their material, further process of diffusional coalescence will lead to usual picture of decomposition. Yet, the very fact of metastability can delay this process leading to long-living nanocrystalline alloy. Similar results had been obtained earlier [7,9,10].

Particularly, in [9] an attempt has been made to take into account the size distribution for nuclei ensemble. Taking a Gaussian distribution, the Gibbs free energy surfaces for different external radii  $R$  have been calculated. The same three possibilities, I - usual decomposition, II - metastable minimum, III - nucleation forbidden has been found.

The competitive nucleation of two intermediate phases in limited volumes is now investigated.



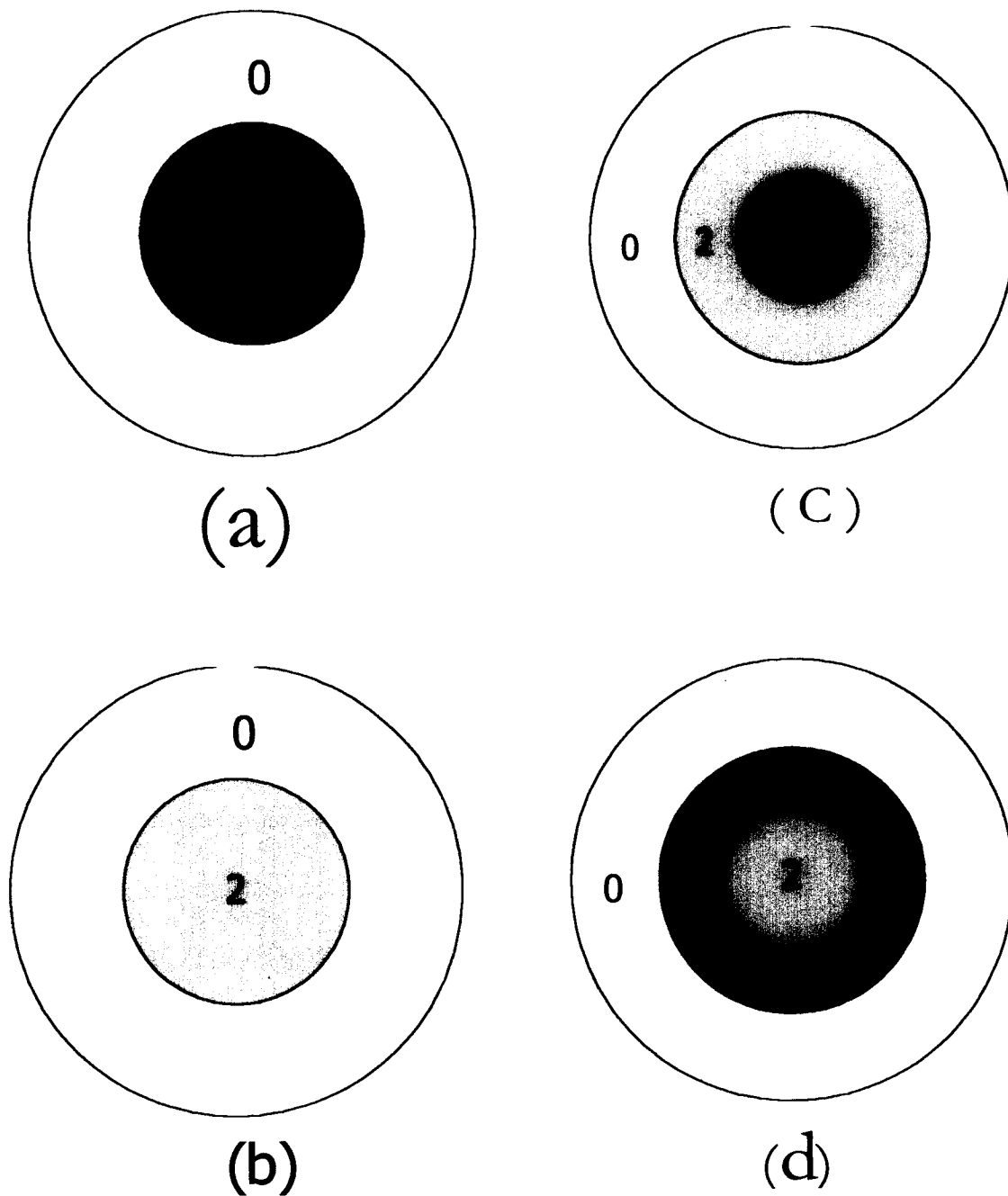


Fig. 4. Modes of nucleation and growth of new phases in the centre of a small particle or a region of supply: (a) – nucleation of phase 1; (b) – nucleation of phase 2; (c), (d) – competitive formation of phase 1 and phase 2.

To investigate the possible evolution paths, the concept of “reaction coordinate” is used. This derives from the method of molecular statics in the microscopic diffusion theory. In this method a “reaction coordinate” is introduced, being defined as a difference between coordinates of migrating atom and the centre of the “gate” through which this atom passes. At every fixed value of the reaction coordinate the system is allowed to relax to the minimal potential energies. Such procedure gives the quasi-equilibrium dependence of these energies on the reaction coordinate. This dependence has a maximum, which is interpreted as activation energy.

In the present study, the role of potential energy is played by the Gibbs energy, and the role of reaction coordinate by the mole fraction of component B in the parent phase.

At every fixed reaction coordinate  $X_m$ , The Gibbs energy is minimised. Naturally, as in the case of molecular static, the following question remains – is such quasi-equilibrium process kinetically possible? But it must be recalled that in the present study, the kinetic aspect is not considered.

To catch the main idea, let the intermediate phases be line compounds with fixed compositions  $X_1$ ,  $X_2$ , and the parent supersaturated phase behaves like an ideal solution (see figure 5):

The Gibbs energy of mixing per atom of the parent supersaturated phase is such:

$$\Delta g_{old}(X) = kT(X \cdot \ln(X) + (1-X) \cdot \ln(1-X)). \quad (7)$$

The expression for the driving force is :

$$\Delta G = nV_1 \cdot \Delta g_1 + nV_2 \cdot \Delta g_2 + n(V - V_1 - V_2) \cdot \Delta g_{old}(X_m) - nV \cdot \Delta g_{old}(X_0) + \Delta G_{surf}. \quad (8)$$

Hereby  $\Delta g_2$  and  $\Delta g_1$  are the isothermal Gibbs energies of formation (per atom) from pure solid components.

The conservation law leads to:

$$X_0 \cdot V = X_1 \cdot V_1 + X_2 \cdot V_2 + X_m \cdot (V - V_1 - V_2), \quad (9)$$

where again the number of atoms per unit volume  $n$  is taken the same in the three phases.

The reaction coordinate  $X_m$  (medium composition) decreases from  $X_0$  in the process of evolution.  $V = \frac{4}{3}\pi R^3$  is the total volume of particle or of the “supply region”.

According to the configurations represented in figure 4 it follows:

$$(a) \quad V_1 = \frac{4}{3}\pi r_1^3, \quad V_2 = 0, \quad \Delta G_{surf} = 4\pi r_1^2 \cdot \sigma_{10}, \quad (10)$$

$$(b) \quad V_1 = 0, \quad V_2 = \frac{4}{3}\pi r_2^3, \quad \Delta G_{surf} = 4\pi r_2^2 \cdot \sigma_{20}, \quad (11)$$

$$(c) \quad V_1 = \frac{4}{3}\pi r_1^3, \quad V_2 = \frac{4}{3}\pi(r_2^3 - r_1^3), \quad \Delta G_{surf} = 4\pi r_1^2 \cdot \sigma_{12} + 4\pi r_2^2 \cdot \sigma_{20}, \quad (12)$$

$$(d) \quad V_1 = \frac{4}{3}\pi(r_1^3 - r_2^3), \quad V_2 = \frac{4}{3}\pi r_2^3, \quad \Delta G_{surf} = 4\pi r_2^2 \cdot \sigma_{21} + 4\pi r_1^2 \cdot \sigma_{10}. \quad (13)$$



State parameters  $r_1$ ,  $r_2$ ,  $X_m$  are linked by conservation law (9). Therefore  $\Delta G$  can be treated as a function of two independent parameters  $\Delta G(r_1, X_m)$  or  $\Delta G(r_2, X_m)$ . Numeric analysis shows that minimisation of  $\Delta G$  at fixed reaction coordinate  $X_m$  gives  $r_1 = 0$  or  $r_2 = 0$ . It means that the three-phase configurations  $\alpha + 1 + 2$  ((c) and (d)) appeared to be less favourable than two-phase configurations  $\alpha + 1$  (a) or  $\alpha + 2$  (b). Therefore, dependencies of  $\Delta G(X_m)$  are presented only for regimes (a) and (b). Results can be gathered into the following three cases:

**Case 1.** When the interface energies are such that  $\sigma_{10} < \sigma_{20}$  with bulk driving force for phase 1 greater than for phase 2, phase 1 has a lower nucleation barrier and its formation is more favorable in general. Then system will stop in absolute minimum state (decomposition  $\alpha + 1$ ). That is the usual case of total suppression of the metastable phase 2 by stable phase 1.

**Case 2.** When  $\sigma_{20} \ll \sigma_{10}$  with bulk driving force for phase 1 larger than for phase 2, nucleation of phase 1 is more difficult.

With the following values of the parameters:  $n = 6 \cdot 10^{28} m^{-3}$ ,  $X_o = 0.05$ ,  $kT = 8.8 \cdot 10^{-21} J$ ,  $R = 1.45 \cdot 10^{-8} m$ , for phase 1:  $\sigma_{10} = 0.6 Jm^{-2}$ ,  $\Delta g_1 = -1.75 \cdot 10^{-20} J$ ,  $X_1 = 0.4$  and for phase 2 correspondently:  $\sigma_{20} = 0.04 Jm^{-2}$ ,  $\Delta g_2 = -1.65 \cdot 10^{-20} J$ ,  $X_2 = 0.5$ , it appears in figure 6 that phase 2 will nucleate first (suppressing the formation of phase 1) and the system will stop in state B ( $\alpha + 2$ ). In this case a small volume helps phase 2 to suppress the precipitation of phase 1. Moreover, it is noteworthy that the absolute minimum of Gibbs energy for phase 2 is being reached during the evolution of reaction coordinate before the correspondent value for phase 1 as represented in figure 6.

For above-mentioned parameters, the nucleation barrier for phase 1 is equal to  $\Delta G = 2.327 \cdot 10^{-17} J$  at point  $X_m = 0.0465$  when the radius of critical nuclei  $r_1 = 3.1 \cdot 10^{-9} m$  and for phase 2 appears to be negligible at the scale chosen in figure 6 ( $\Delta G = 3.15 \cdot 10^{-20} J$  when  $r_2 = 4 \cdot 10^{-10} m$ ). Minimal values are for phase 1:  $\Delta G = -3.82 \cdot 10^{-17} J$ ,  $X_m = 0.017$ ,  $r_1 = 6.4 \cdot 10^{-9} m$ , for phase 2:  $\Delta G = -5.88 \cdot 10^{-17} J$ ,  $X_m = 0.0257$ ,  $r_2 = 5.4 \cdot 10^{-9} m$  (point B in figure 6).

Note that a greater value of  $\sigma_{10}$  is consistent with a greater driving force for the formation of phase 1 as generally stronger negative Gibbs energy of formation (as for phase 1) yields higher value of the interface energy. Furthermore, smaller value of the interface energy for phase 2 is consistent with higher frequency of nucleation favoring small supply regions capable to set up a metastable state.



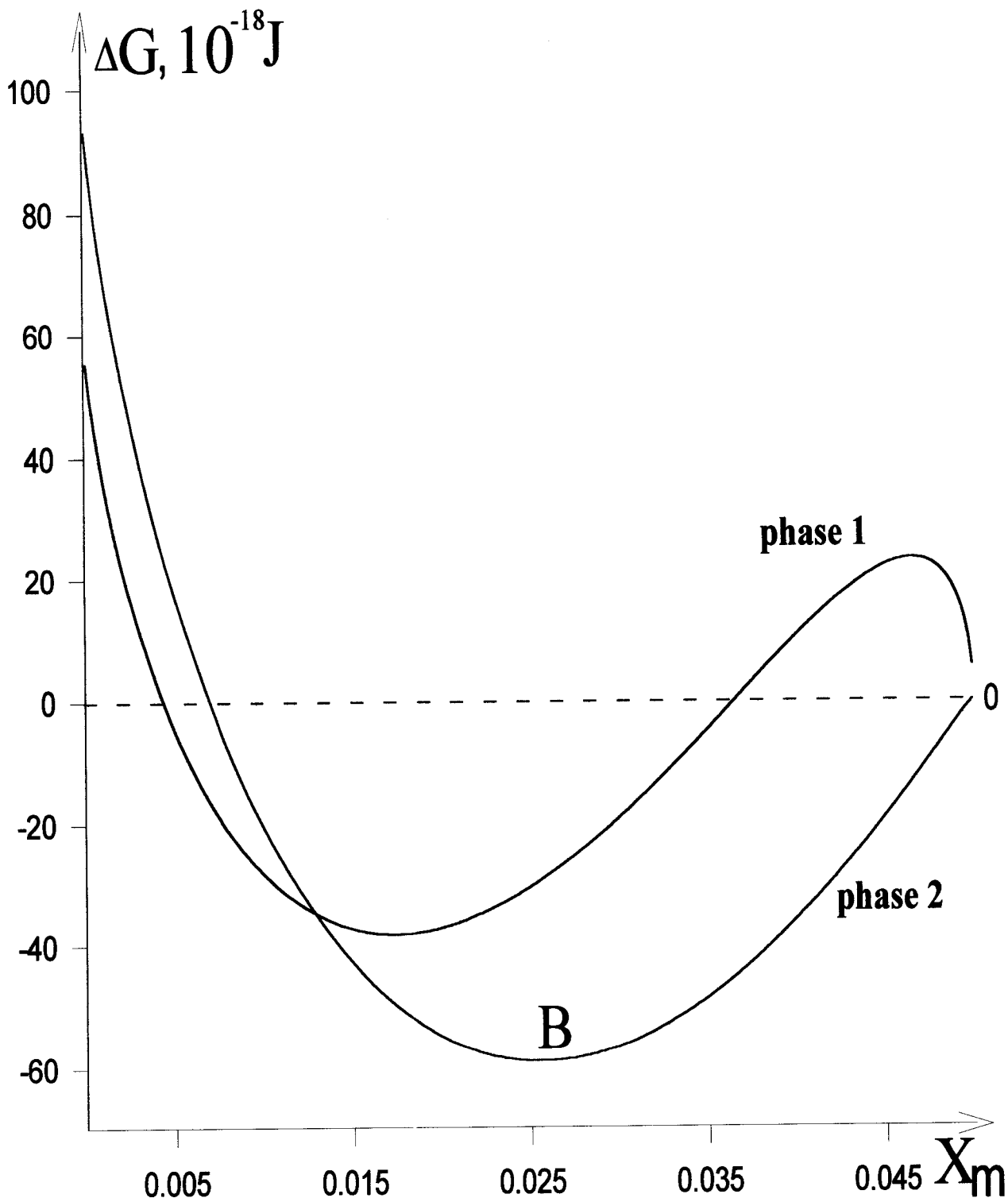


Fig. 6. Gibbs free energy dependencies on depletion of parent phase - cases (a) and (b). Parameters are given in the main text. Note that the evolution proceeds with decreasing mole fraction  $X_m$  in the parent phase, (which corresponds to direction from the right to the left).

**Case 3 or crossover regime.** When the conditions  $\sigma_{20} < \sigma_{10}$  with a driving force for phase 1 larger than for phase 2 are satisfied the following other situation can be set up: Nucleation remains easier for phase 2 but with a minimum of Gibbs energy for phase 1 being deeper than for phase 2 but this for a greater depletion (smaller  $X_{med}$ ). Then, a cross over from regime (a) to regime (b) becomes possible. This case is represented in figure 7 obtained with the following parameters:  $n=8.5 \cdot 10^{28} m^{-3}$ ,  $X_o=0.04$ ,  $kT=8 \cdot 10^{-21} J$ ,  $R=1.2 \cdot 10^{-8} m$ , for new phases  $\sigma_{10} = 1.2 Jm^{-2}$ ,

As represented in figure 7 this yields a nucleation barrier equal to  $MN = 2.6 \cdot 10^{-17} J$  (for phase 1), and  $KP = 6.1 \cdot 10^{-18} J$  (for phase 2), bottom depths are equal to  $AF = -1.37 \cdot 10^{-16} J$ , (for phase 1) and  $BE = -4.66 \cdot 10^{-17} J$  (for phase 2). Point S is a crossover point at which  $X_m = 0.027325$ ,  $\Delta G = -2.255 \cdot 10^{-17} J$ .

If this additional barrier  $\Delta G_{12}$  is small enough, so that  $\Delta G_{12} + KP < MN$  then the evolution path of the formation of the phase 1 via phase 2 becomes more favorable and phase 2 helps to form phase 1.

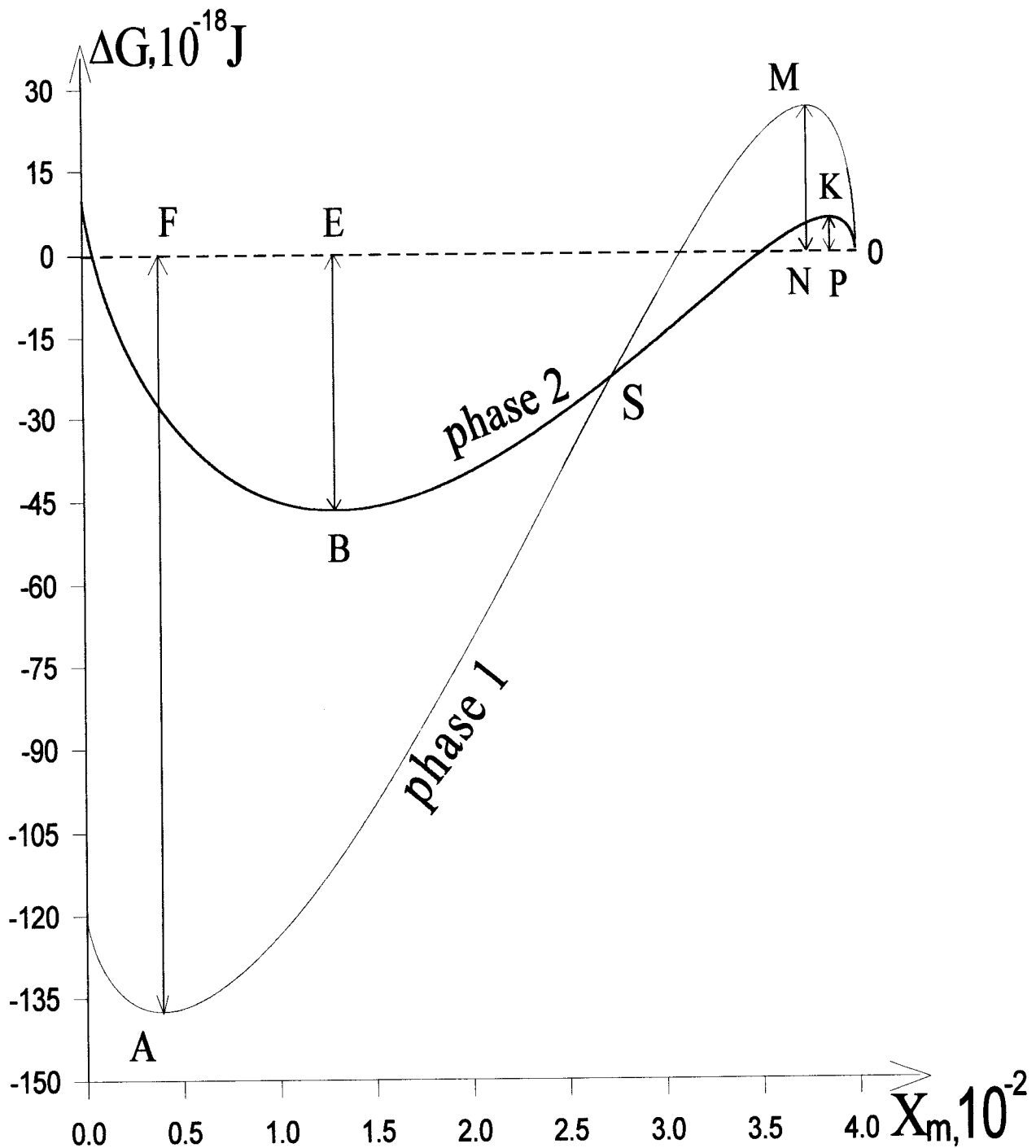


Fig 7. Gibbs energy dependence on depletion of matrix in crossover regime. Nucleation barrier KP for phase 2  $\Delta G = 6.1 \cdot 10^{-18} J$  when  $X_m = 0.0386$  and  $r_2 = 1.73 \cdot 10^{-9} m$ , and for phase 1  $\Delta G = 2.6 \cdot 10^{-17} J$ ,  $X_m = 0.0374$ ,  $r_1 = 2.32 \cdot 10^{-9} m$ . Minimal value: for phase 2  $\Delta G = -4.66 \cdot 10^{-17} J$ , hereby  $X_m = 0.013$ ,  $r_2 = 4.56 \cdot 10^{-9} m$ , and for phase 1  $X_m = 0.0039$ ,  $r_1 = 5.4 \cdot 10^{-9} m$ .

It is now of interest to study, through a practical example, whether a metastable state, at the sample level, can be attained owing to a very high nucleation frequency and how such a metastable state may compete with the formation of the stable phase.

#### IV. Application to Precipitation of the Ordered Compound $Al_3Li$ in Supersaturated $AlLi$ Solid Solution

Decomposition of supersaturated solution of Li in Al usually leads to a dispersion of coherent precipitates of metastable phase  $Al_3Li$  within the disordered matrix which hinders subsequent transformation into the stable phase  $AlLi$ .

From a qualitative point of view, this behaviour is mainly due to the coherence between metastable phase and the matrix yielding a small interface energy. The following development is an attempt to give a quantitative approach to this phenomenon.

The parent phase in the solution  $AlLi$  has the following Gibbs free energy of formation [11]:

$$N_A \cdot \Delta g_{old}(X) = \left\{ R \cdot T \cdot (X \ln(X) + (1-X) \ln(1-X)) + X(1-X) \left\{ (8T - 2700) + (1-2X)10^{-6} + (1-2X)^2(0.1T + 3000) \right\} \right\} \quad (12)$$

In eqn. (14)  $\Delta g_{old}(X)$  is the Gibbs energy of formation (per atom) of the disordered solid solution.  $N_A$  is the Avogadro number,  $R = k/N_A$ .

The expression for the Gibbs energy of formation of phase  $AlLi$  is given by [11]:

$$N_A \cdot \Delta g_1 = -41300 + 16.86T \quad (15)$$

The Gibbs energy of formation of the metastable phase  $Al_3Li$  is [12]:

$$N_A \cdot \Delta g_2(X_2) = N_A \cdot \Delta g_{old}(X_2) - \Delta \omega \quad (16)$$

$\Delta \omega > 0$ , determines the "Gibbs energy advantage" of  $Al_3Li$  with respect to the parent phase. Unfortunately, data from different sources are contradictory and may lead to thermodynamic instability of  $Al_3Li$  [11]. To guarantee the decrease of the driving force with increasing temperature, we have used only data, which lead to metastability at low temperatures. Our estimates have shown that a decrease of temperature makes the stabilization of the metastable phase more probable [12]. The value  $\Delta \omega$  is different for different temperatures and increase with the decreasing of the temperature.

Using the following data:  $n = 6.025 \cdot 10^{28} m^{-3}$ ,  $X_0 = 0.2$ ,  $T = 600K$ ,  $R = 1.5 \cdot 10^{-9} m$ , for phase  $AlLi$ :  $\sigma_{10} = 0.314 Jm^{-2}$ ,  $X_1 = 0.5$  and for phase  $Al_3Li$ :  $\sigma_{20} = 0.014 Jm^{-2}$ ,  $X_2 = 0.25$ ,  $\Delta \omega = 900 J/mole$ , the Gibbs energy has been calculated and represented in figure 8.

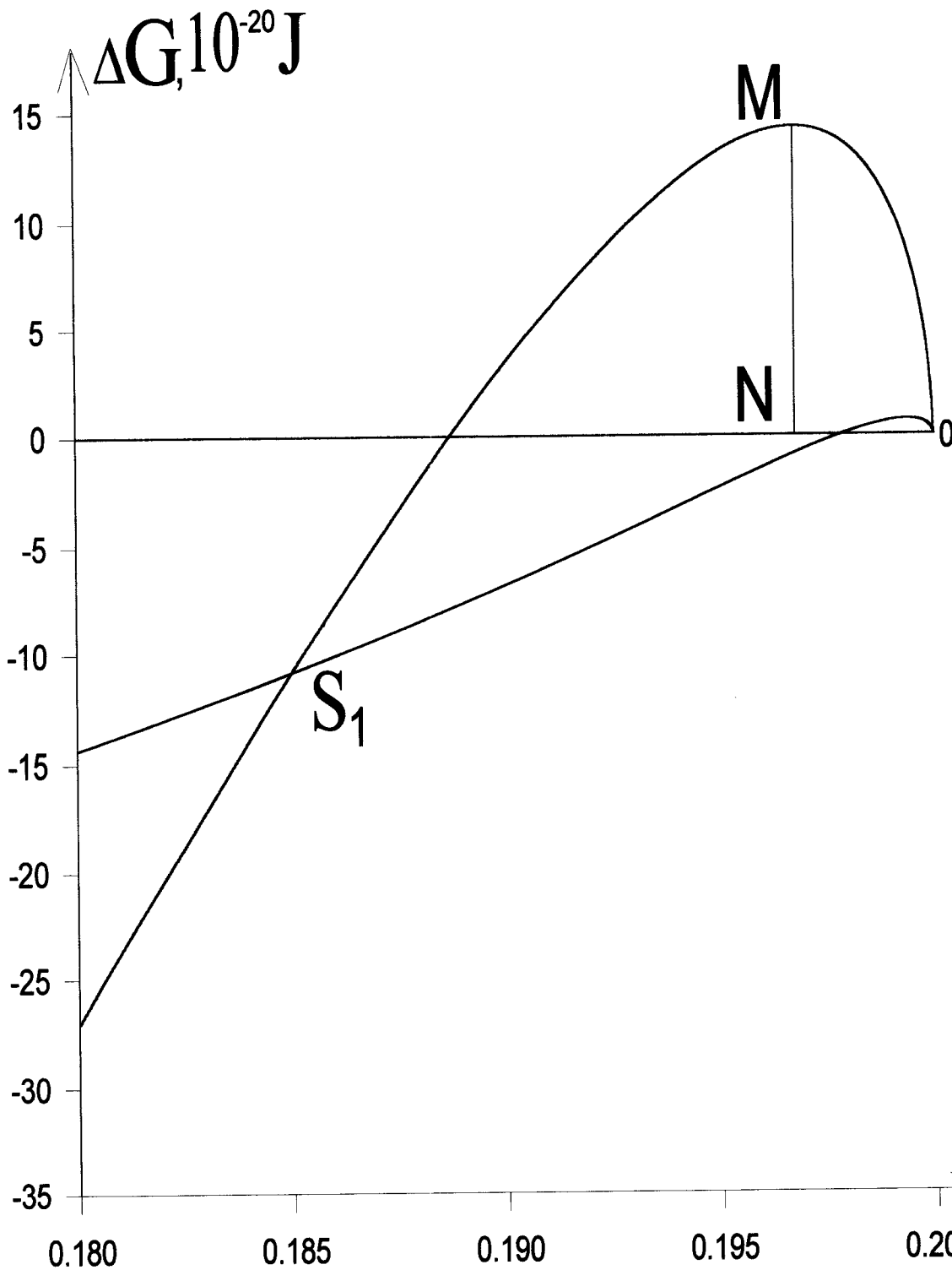


Fig. 8. Gibbs energy dependence on depletion of matrix for AlLi system in crossover regime. Parameters are given in the main text. Point  $S_1$  is the crossover point.

It appears from figure 8 that there is a cross over effect. This yields a nucleation barrier for phase 1  $MN = 14.28 \cdot 10^{-20} J$  with the critical radius  $r_1 = 3.35 \cdot 10^{-10} m$ , and correspondently for phase 2  $KP = 0.694 \cdot 10^{-20} J$  and  $r_2 = 3.5 \cdot 10^{-10} m$ . Though the Gibbs energy barrier for the formation of  $Al_3Li_1$  remains smaller than for phase  $Al_1Li_1$  ( $KP \ll MN$ ), the critical radius for phase  $Al_3Li_1$  is found to be greater than for the stable phase  $Al_1Li_1$  ( $r_2 > r_1$ ) in the high temperature range. But, due to the increase of the driving force when temperature is lowered, metastable phase becomes more favorable in the lower temperature range. For example when  $T = 500K$  yields  $r_1 > r_2$ .

Point  $S_1$  is the crossover point at which  $X_m = 0.185035$ ,  $\Delta G = -10.8257 \cdot 10^{-20} J$  and it corresponds to  $r_2 = 9.195 \cdot 10^{-10} m$  ( $r_1 = 0$ ) at the beginning of transformation  $\alpha + 2 \rightarrow \alpha' + 1$ . Provided that the unknown energy barrier  $\Delta G_{12}$ , mainly controlled by the interface energy between phase 1 and phase 2, is overpassed, the transformation of phase 2 in phase 1 could be possible. However, experiment shows that precipitates of the incoherent stable phase  $Al_1Li_1$  are only found at the grain boundary. This suggests that a too high interface energy  $\sigma_{12}$  (between  $Al_3Li_1$  and  $Al_1Li_1$ ) may hinder subsequent transformation from metastable phase  $Al_3Li_1$  to stable phase  $Al_1Li_1$ .

## Summary

It has been shown from thermodynamics that nucleation in nanometric volumes as in very small single particles or when multiple simultaneous nucleation with short distance between the nucleation sites occurs, nucleation can be totally suppressed due to depletion of the parent phase.

Furthermore when two phases compete for nucleation and growth the following regimes has been found to depend on supply region size (or particle size) and thermodynamic parameters of parent and intermediate phases: (i) total prohibition of separation for both phases, (ii) formation and stabilization of metastable phase

instead of stable one, (iii) relative stabilization of metastable phase with the temporary delay of its transformation into the stable phase after certain crossover point (in the case of sufficiently high additional barrier for next transformation), (iv) formation and growth of stable phase, when the metastable phase does not appear at all, (v) formation and growth of stable phase via the metastable phase.

Application to phase transformation in supersaturated solid solution AlLi gives results in qualitative agreement with experiment where a dispersion of metastable  $Al_3Li$  precipitates is found within the disordered solution.

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