Review

N. N. SIROTA

Hydromelioration Institute, Moscow, USSR

Certain Problems of Polymorphism (II)[1]
Generalized Clausius-Clapeyron Equation
and Ostwald's Step Rule

Contents

[1] Part II was read at the crystallography colloquium in Karl-Marx-University, Leipzig, and partly in Humboldt University, Berlin, GDR, in December 1980. Part I: Cryst. Res. Technol. 17, No 6, 661 – 691 (1982) (hereafter Sirota I).

Introduction

Problems of polymorphic transitions caused by the variation of external generalized forces (pressure, magnetic, electric, gravitational fields, surface energy, etc.), and of origination of new phases from thermodynamically supersaturated initial phase, are of major interest and are playing an ever-increasing role in coping with numerous practical tasks in modern technique and technology. The former president of the Academy of Sciences of the USSR A. P. Alexandrov also paid attention to the actuality of these problems.

The study of the influence of external forces and fields upon relative supersaturation and the kinetics of phase transitions, together with the investigation of mechanisms and kinetics of occurrence of metastable phases in chemical reactions of crystallization, transformations in solids and heat treatment processing of different alloys are directly connected with the problems denoted above and acquire great theoretical and practical interest.

In this context a special principal importance has comprehension, substantiation, interpretation and further development of the famous Ostwald's step rule (Ostwald) according to which in none of processes the most stable phase is attained at once but first appears the neighbouring condition which is the least stable of all the possible states.

However, now it has become clear that this important rule is not of a general character but is realized under some certain conditions.

Later on we shall consistently consider the relation of generalized Clausius-Clapeyron equation to Ostwald's step rule, and find the factors determining the value of relative thermodynamic supersaturation and the dependence on it of the rate of formation and growth of stable and metastable-phase nuclei. We shall consider conditions of formation of metastable phases in particular in isothermal transformations, and study the influence they exert upon the kinetics of isothermal phase transitions.

Analysis of these questions permits to find quite strictly the limits of Ostwald's step rule applicability.

I. Generalized Clausius-Clapeyron Equation

W. Ostwald was the first to translate the work of J. W. Gibbs "On the Equilibrium of Heterogeneous Substances" into German, having supplied it with rather interesting comments and a foreword. In fact only after the publication of this translation by Ostwald the works of Gibbs became available to European reader. The publications of J. C. Maxwell also helped in spreading of Gibbs' ideas.

Let's remark that the first translation into Russian appeared in the USSR, edited by V. K. Sementchenko in 1950.

According to adopted classification based on Gibbs' thermodynamic method, first-order phase transitions are those with non-zero latent heat of transformation, e.g. a transition in one-component substance at constant pressure and constant temperature, when in compliance with the Gibbs' rule there are no degrees of freedom stipulated by external factors. Conversely, non-first (second) order phase transitions under the same external conditions take place without releasing or absorbing latent heat; in their nature they do not correspond to non-variant equilibrium under similar conditions. Formally non-first-order (second order) transitions can be treated as those with additional internal degrees of freedom.

Thermodynamic theory of second-order phase transitions has been studied from different view-points by EHRENFEST, LANDAU (1937), LANDAU and LIFSHITZ, GINZBURG, KHACHATURIAN, VONSOVSKII, SEMENTCHENKO, LEONTOVITCH, K. P. BELOV, SIROTA, SMOLENSKII and others. An original, though incomplete, review has been done by STANLEY. Let's remark that in particular range of thermodynamic supersaturations, the phase transitions of first and second order are similar concerning the kinetics of the processes.

In the study of problems of polymorphism, finding out the conditions of formation and stability of stable and metastable polymorphic modifications the application of Gibbs' thermodynamic method is useful and, possibly, even inevitable.

In case of the first-order phase transition when there are two phases in equilibrium in a one-component system, the variation of Gibbs' free energy is zero[2]), $\Delta Z_{1,2} = 0$, and consequently for the phases 1 and 2

$$dZ_1 = dZ_2 \,.$$

Gibbs free energy is a characteristic function of generalized forces X_i — temperature, pressure, magnetic, and electric fields — and the mole number n_j,

$$Z = Z(T, X_i, n_j) \equiv Z(T, p, \mathcal{H}, \mathcal{E}, n, ...) \,,$$

and so

$$dZ_1 = \left(\frac{\partial Z_1}{\partial T}\right) dT + \sum_i \frac{\partial Z_1}{\partial X_i} dX_i + \sum_j \frac{\partial Z_1}{\partial n_j} dn_j \,,$$

$$dZ_2 = \left(\frac{\partial Z_2}{\partial T}\right) dT + \sum_i \frac{\partial Z_2}{\partial X_i} dx_i + \sum_j \frac{\partial Z_2}{\partial n_j} dn_j \,,$$

where $\frac{\partial Z}{\partial X_i} = x_i$ are generalized coordinates[3]), $\frac{\partial Z}{\partial n_j} = \mu_j$ are chemical potentials.

From these equations for one-component substance with constant mole number, $n_j = $ const we infer that the derivative of temperature with respect to any other generalized force X_q along equilibrium line is:

$$\frac{dT}{dX_q} = - \frac{\dfrac{\partial(Z_1 - Z_2)}{\partial X_q} + \sum_{i \neq q} \dfrac{\partial(Z_1 - Z_2)}{\partial X_i} \dfrac{\partial X}{\partial X_i}}{\partial(Z_1 - Z_2)/\partial T} \,.$$

This equation may be considered as generalized Clausius-Clapeyron equation.

In contrast to the above equation when many of the generalized forces are changing simultaneously (e.g. temperature varies together with pressure and magnetic field intensity) the study of the functional dependences is overcomplicated.

However, quite clear consideration is possible to be conducted in different sections of the multi-dimensional space when all the generalized forces but two of them are constant.

For example, when T and X_q are changing and all the other forces are constant $(X_{i \neq q} = $ const, $dX_{i \neq q} = 0)$, then

$$\frac{dT_k}{dX_q} = - \frac{x_{1q} - x_{2q}}{S_1 - S_2} \,.$$

---

[2]) Presently Gibbs' free energy is as a rule denoted G; we conserve the notation Z as in part I, which was earlier adopted in German.

[3]) Such are, for example, entropy S, volume V, electric $\left(\dfrac{1}{4\pi} D\right)$ and magnetic induction $\dfrac{1}{4\pi} B$, etc. (e.g. see SEMENTCHENKO, 1968; BAZAROV).

Here $S_1 - S_2$ is the difference of entropies of phases 1 and 2 at $T = T_k$, equal to the difference of enthalpies divided by the transition temperature:

$$S_1 - S_2 = \frac{H_1 - H_2}{T_k},$$

then

$$\frac{dT_k}{dX_q} = -T_k \frac{x_{1q} - x_{2q}}{H_1 - H_2},$$

or

$$\frac{d\ln T_k}{dX_q} = -(x_{1q} - x_{2q})/(H_1 - H_2).$$

When pressure is changing $(X_q = p,\ x_q = V)$, the above equation acquires the form:

$$\frac{d\ln T_k}{dp} = -(V_1 - V_2)/(H_1 - H_2)_p.$$

When magnetic field strength is changing $\left(X_q = \mathcal{H},\ x_q = -\dfrac{\mathcal{H} + 4\pi\mathcal{M}}{4\pi}\right)$,

$$\frac{d\ln T_k}{d\mathcal{H}} = (M_1 - M_2)/(H_1 - H_2).$$

When the electric field strength is changing $\left(X_q = \mathcal{E},\ x_q = -\dfrac{\mathcal{E} + 4\pi P}{4\pi}\right)$,

$$\frac{d\ln T_k}{d\mathcal{E}} = (P_1 - P_2)/(H_1 - H_2).$$

Here P is polarization, M is magnetization. When two of the generalized forces X_p and X_q are varying but temperature T, together with all the other forces, is constant then

$$\frac{dX_p}{dX_q} = -\frac{\dfrac{\partial(Z_1 - Z_2)}{\partial X_q}}{\dfrac{\partial(Z_1 - Z_2)}{\partial X_p}} = (x_{1q} - x_{2q})/(x_{1p} - x_{2p}).$$

For example,

$$\frac{dp_k}{d\mathcal{H}} = \frac{M_1 - M_2}{V_1 - V_2};\quad \frac{dp_k}{d\mathcal{E}} = \frac{P_1 - P_2}{V_1 - V_2};\quad \frac{\partial\mathcal{H}_k}{\partial\mathcal{E}} = -\frac{P_1 - P_2}{M_1 - M_2}$$

Let us analyse the behaviour of the Gibbs free energy curves of the phases 1, 2 near their mutual equilibrium using the methods of geometrical thermodynamics supposing that external generalized forces are changing (MLODZEYEVSKII 1922, 1937, 1948, 1956; SIROTA 1968). Gibbs free energy of any phase is a characteristic function of generalized forces, including temperature, and a mole number n_j of each component, so that

$$dZ = -S\,dT + \sum x_i\,dX_i + \sum_j \mu_j\,dn_j.$$

In case of one-component substance

$$dZ = -S\,dT + \sum_i x_i\,dX_i.$$

When one of the generalized forces X_i is changing this equation describes the peculiarities of the free energy curve as a function of this force.

The total entropy S is always positive and so its first-order derivative is dS/dT $= c_p/T > 0$. Consequently, $dZ/dT < 0$. The second-order derivative $\partial^2 Z/\partial T^2 < 0$, so the curve Z versus T is falling, its convexity being directed off the abscissa axis.

Quite similar analysis with respect to other generalized forces shows that

$$\frac{\partial Z}{\partial p} > 0; \quad \frac{\partial^2 Z}{\partial p^2} < 0; \quad \frac{\partial Z}{\partial \mathcal{H}} < 0; \quad \frac{\partial^2 Z}{\partial \mathcal{H}^2} < 0; \quad \frac{\partial Z}{\partial \mathcal{E}} < 0; \quad \frac{\partial^2 Z}{\partial \mathcal{E}} < 0 .$$

II. Change of the generalized coordinates in the phase transition in equilibrium.
Thermodynamic supersaturations caused by the deviation of the generalized forces from their equilibrium values

When one of the generalized forces deviates from thermodynamic equilibrium, corresponding, e.g., to non-variant two-phase equilibrium of one-component system, a certain thermodynamic supersaturation is achieved, characterized by the magnitude of the difference $\Delta Z_{12} = Z_1 - Z_2$ of specific Gibbs free energies of phases 1, 2.

In case of non-variant two-phase thermodynamical equilibrium of one-component system $\Delta Z_{12} = 0$. In particular, when $p = \text{const}$ the change of specific entropy $\Delta S_{12} = S_1 - S_2$ in this case is equal to the ratio of phase transition heat $\Delta H_{12} = H_1 - H_2$ to the equilibrium temperature T_k:

$$\Delta S = \frac{\Delta H_{12k}}{T_k} = \frac{\Delta H_{012}}{T_k} + \frac{1}{T_k} \int_0^{T_k} (C_{p1} - C_{p2})\, dT = \int_0^{T_k} \frac{C_{p1} - C_{p2}}{T}\, dT .$$

Note that entropy and enthalpy of high-temperature phase are always higher than corresponding quantities for low-temperature phase,

$$S_2 > S_1; \qquad H_{2k} > H_{1k} .$$

For the two-phase equilibrium of one-component substance at $T = \text{const}$, $p = p_k$, $\Delta Z_{12} = 0$ and the difference of specific volumes $\Delta V_k = V_1 - V_2$ is non-zero. In the situation of transition induced by the change of the pressure, the phase 1 of lower pressure, stable at $p \leqq p_k$ has in accordance with Le Chatelier rule, specific volume greater than the higher-pressure phase 2, stable at $p \geqq p_k$, i.e.

$$V_1 = (\partial Z_1/\partial p)_{pk} > V_2 = (\partial Z_2/\partial p)_{pk} .$$

In this case, as $p_k(V_1 - V_2)_k = -\Delta H_k$ when $T = T_k$, $p = p_k$,

$$\Delta V_{12k} = -\frac{\Delta H_k}{p_k}.$$

In the general case of one-component substance, phase transition being induced by the change of any of the generalized forces X_i in equilibrium $\Delta Z_{12} = 0$ and, taking into account that $\dfrac{\partial Z}{\partial X_i} = x_i$, the equation holds:

$$(x_{1i} - x_{2i}) = -\frac{\Delta H_{12k}}{X_{ik}}$$

or

$$(\overline{\chi}_{1i} - \overline{\chi}_{2i})_k = \Delta H_k / X_{ik}^2 ,$$

where $(x_{1i} - x_{2i})_k / X_{ik} = (\overline{\chi}_{1i} - \overline{\chi}_{2i})_k$ is the difference of generalized mean susceptibilities of phases 1, 2. Here $\Delta H_k \equiv \Delta H_{12k}$ is the enthalpy of the phase transition caused by the change of the generalized force X_i taken at its equilibrium value X_{ik}.

From this follows that in equilibrium of one-component substance (characterized by T_k, p_k or X_k) the change of entropy is equal to the product of the difference of generalized coordinates by the ratio of varying generalized force to the transition temperature,

$$\Delta S_k = -\frac{\Delta x_{ik}}{T_k}\, X_{ik}\,.$$

In particular, when three of the quantities characterizing equilibrium are known, this relation permits to find the fourth quantity.

The value of thermodynamic supersaturation of one-component substance, when one of the generalized forces X_i deviates from equilibrium value X_{ik}, equals to

$$\Delta Z = \Delta Z_k + \int \left(\frac{\partial\,\Delta Z_{12}}{\partial X_i}\right) dX_i + \dots\,.$$

When the deviation from equilibrium is relatively small, the magnitude of thermodynamic supersaturation ΔZ may be represented as a series (SIROTA 1971):

$$\Delta Z_{12} = \left(\frac{\partial\,\Delta Z_{12}}{\partial X_i}\right)\Delta X_{ik} + \left(\frac{\partial^2\,\Delta Z_{12}}{\partial X_i^2}\right)\frac{\Delta X_{ik}^2}{2} + \dots$$

$$\Delta Z_{12} = (x_{1i} - x_{2i})\,(X_i - X_{ik}) + \left[\frac{\partial(x_{1i} - x_{2i})}{\partial X_i}\right]\frac{(X_i - X_{ik})^2}{2 + \dots\,.} + \dots$$

Undoubtedly the subject of substantial interest is the determination of thermodynamic supersaturation value not only with respect to initial equilibrium phase, but to all possible non-equilibrium phases (modifications) of a given substance. To evaluate the magnitude of thermodynamic supersaturation we may use formulae given above, substituting the equilibrium magnitudes of generalized forces X_k by their values for quasi-equilibrium transitions, corresponding to metastable phases.

Leaving only the first term of the series, we find that specific thermodynamic supersaturation of one-component substance equals to the product of the deviation of the generalized force X by the difference of conjugate specific generalized coordinates of phases 1, 2. Using the value of this product given above we find:

$$\Delta Z = (x_{1i} - x_{2i})\,(X_{ik} - X_i) \cong -\Delta H_k(\bar{\chi}_{1i} - \bar{\chi}_{2i})\,X_i X_{ik} \cong -\frac{X_{ik} - X_i}{X_{ik}}\,\Delta H_k\,.$$

Note that

$$X_i X_{ik} \approx X_{ik}^2; \qquad \Delta H_k \equiv \Delta H_{12k}\,.$$

Thus thermodynamic supersaturation is equal to: in case of undercooling:

$$\Delta Z_T = -(S_1 - S_2)\,(T_k - T) \cong -\Delta H_k + \left(\frac{C_{p1}}{T_k} - \frac{C_{p2}}{T_k}\right)T_k^2 \cong \frac{\Delta H_k(T_k - T)}{T_k}\,;$$

when pressure is changing:

$$\Delta Z_p = (V_1 - V_2)\,(p_k - p) \cong -\Delta H_k - (\bar{\chi}_{p1} - \bar{\chi}_{p2})\,p_k^2 \cong -\frac{p_k - p}{p_k}\,\Delta H_k\,;$$

when magnetic field strength is changing

$$\Delta Z_{\mathscr{H}} = (M_1 - M_2)\,(\mathscr{H} - \mathscr{H}_k) \cong -\Delta H_k + (\bar{\chi}_{\mathscr{H}1} - \bar{\chi}_{\mathscr{H}2})\,\mathscr{H}^2 \cong \frac{\mathscr{H}_k - \mathscr{H}}{\mathscr{H}_k}\,\Delta H_k\,;$$

when electric field strength is changing

$$\Delta Z_{\mathscr{E}} = (P_1 - P_2)\,(\mathscr{E} - \mathscr{E}_k) \cong -\Delta H_k + (\bar{\chi}_{\mathscr{E}1} - \bar{\chi}_{\mathscr{E}2})\,\mathscr{E}_k^2 \cong \frac{\mathscr{E}_k - \mathscr{E}}{\mathscr{E}_k}\,\Delta H_k\,,$$

where M is intensity of magnetization, P — polarization, $\chi_i = \dfrac{\partial x_i}{\partial X_i}$; $\chi_i = \dfrac{x_i}{x_i}$ true and average generalized susceptibilities.

As follows from the right sides of the given equations, the values of thermodynamic supersaturation for one-component substances to a first, linear approximation are equal to the difference of enthalpies plus the product of the difference of average generalized susceptibilities by the square of the conjugate generalized force. On the other hand

$$\Delta Z = -\Delta H_k \frac{\Delta X_k}{X_k} = -\Delta S \frac{\Delta X_k}{X_k} T_k \,,$$

i.e. the value of specific thermodynamic supersaturation is proportional to the product of the transition heat by relative deviation of the generalized force from the non-variant equilibrium value.

III. Thermodynamic supersaturation in two- and multi-component systems

Thermodynamic supersaturation in two and multi-component systems may be calculated in geometric thermodynamic approximation of the regular-solution theory, in quasi-chemical and other approximations.

Using the methods developed earlier (BECKER; BORELIUS; PINÉS 1941, 1961; DANILOV, KAMENETSKAYA; SIROTA (1944, 1948, 1955, 1970); IVANOV), based on a semi-empirical interpretation of ROSEBOOM and VAN-LAAR's method (see also URAZOV; TAMMANN 1924; VOGEL; MLODZEYEVSKII 1922, 1947; ANOSOV, POGODIN; ANOSOV et al.; DEHLINGER; HUME-ROTHERY and REYNOR; DARKEN and GURRY; LUMSDEN; PAUFLER; PAUFLER, LENCHNER) one can find quantitatively the elements of phase diagram — liquidus and solidus lines and surfaces, limits of existence of solid solutions — and also determine the magnitude of thermodynamic supersaturation in case of different undercoolings, composition changes, or when generalized forces deviate from their equilibrium values.

Temperature dependence of the concentration limit of existence of solid solution of α in the basic component A, from which, as the temperature falls, chemical compound $A_m B_n(\gamma)$ with concentration C_γ is precipitated, may be determined from phase equilibrium condition, i.e. equality of chemical potentials of phases α and γ at given temperature and pressure:

$$\mu_A^\alpha = \mu_A^\gamma; \qquad \mu_B^\alpha = \mu_B^\gamma \,.$$

This equilibrium condition is equivalent to a system of equations:

$$\frac{\partial Z_\alpha}{\partial C} = \frac{\partial Z_\gamma}{\partial C} \; ; \quad Z_\alpha - Z_\gamma = (C_\gamma - C_\alpha) \frac{\partial Z_\alpha}{\partial C} \,.$$

In the approximation of the theory of solutions with different degrees of regularity (GUGGENHEIM; SIROTA; CHRISTIAN) the free energy of two-component solid solution α is

$$Z_\alpha = Z_A + (Z_B - Z_A) C_\alpha + K_\alpha C_\alpha (1 - C_\alpha) + RT[C_\alpha \ln C_\alpha + (1 - C_\alpha) \ln (1 - C_\alpha)].$$

In general in this case interaction coefficient of the components in the solution, K_α depends on temperature and composition (PINÉS; SIROTA 1948, 1970). Thus

$$K_\alpha = K_{0\alpha}'(1 + \varkappa_\alpha T)(1 + \lambda C_\alpha) \cong K_{0\alpha}'[1 + \lambda C_\alpha]a = K_{0\alpha}'(P + QT) =$$
$$= K_{0\alpha}(1 + \lambda C_\alpha) \,.$$

Here

$$a = 1 + \varkappa_\alpha T; \qquad P = 1 + \lambda_\alpha C_\alpha; \qquad Q = \varkappa_\alpha P \ .$$

Neglecting concentrational and temperature dependences of K_α we have:

$$\frac{\partial Z_\alpha}{\partial C} = (Z_B - Z_A) + K_\alpha(1 - 2C_\alpha) + RT \ln \frac{C_\alpha}{1 - C_\alpha}.$$

Proceeding from the phase equilibrium equation and considering C_γ to be a constant, when solubility is small, $C_\alpha \to 0$, we obtain an approximate expression (assuming that components don't dissolve in compound γ):

$$\ln C_\alpha = -[K_\alpha + Z_B - Z_A + 1/C_\gamma(Z_A - Z_\gamma)]/RT \ .$$

The corresponding supersaturations are

$$\Delta Z_{\Delta T} \cong RT_1 \ln C_\alpha(T_2)/C_\alpha(T_1) \ .$$

At present this method of geometric thermodynamics is widely used for different computer calculations of phase diagrams (see. e. g. KAUFMAN, BERNSTEIN).

Let us consider another example: the existence of continuous solid solution and its spinodal decay.

When interaction coefficient is negative, $K_\alpha < 0$, continuous solid solution will be thermodynamically stable at all temperatures, whereas in the entire concentration region will be $K_\alpha < 0$ and the curve free energy versus composition will not have inflection points and several extrema.

When the coefficient of interaction of the components in solid phase is positive, $K_\alpha > 0$, lower than a certain temperature T_k two-phase decay of the solid solution into phases α_1, α_2 takes place; the concentration boundaries of the decay in symmetrical case are described by the equation

$$RT \ln \frac{1 - C_{\alpha 2}}{1 - C_{\alpha 1}} = K_{0\alpha}[(\lambda - 1)(C_{\alpha 2}^2 - C_{\alpha 1}^2) - 2\lambda(C_{\alpha 2}^3 - C_{\alpha 1}^3)] \ .$$

Hence, using L'Hopital rule, at $C_{\alpha 1} = C_{\alpha 2} = C_{ak}$ we find the critical temperature: $T_k = \dfrac{2K_0}{R}[(\lambda - 1) - 6\lambda C_{\alpha k}](1 - C_{\alpha k})^2$; at higher temperatures continuous solid solution exists.

The boundary of heterogeneous region at $C_{\alpha 1} \to 0$ in this case is described by the equation:

$$\ln(1 - C_{\alpha 2}) = -K_{0\alpha}(\lambda + 1)/(RT) \ .$$

This equation is in its form similar to that of SHREDER, derived and analysed by ANOSOV (1953).

Under this condition the value of thermodynamic supersaturation of the solid solution at the temperature falling from T_2 to T_1 is defined by the expression (concentrations are supposed to be small and phase boundary is plane):

$$\Delta Z_{21} = K_{0\alpha}(\lambda + 1)(T_2 - T_1)/T_2 \ .$$

IV. Thermodynamic supersaturation caused by light, radiation and other external actions

A problem of special interest is the study of residual influence of penetrating radiation (electromagnetic, light, ultrasonic irradiation) and also the influence of residual cold plastic deformation upon the value of thermodynamic supersaturation.

Penetrating radiation action, plastic deformation and other kinds of excitation create, as a rule, non-uniformly distributed state with an increased value of Gibbs free energy. All sorts of excitation cause non-uniformity of state also because of different local defects each of them having its relaxation time.

If we confine ourselves only to mean values of Gibbs free energy, then averaged value of thermodynamical supersaturation at any temperature is determined by specific absorbed energy in the process of external action. In one-component substances it leads to the change of phase transition temperature (see SIROTA I).

In case of limited-region solid solution subject to external action, the increase of its specific Gibbs free energy causes the shift of miscibility gap (i.e. change of solubility of isolating surplus phase, SIROTA 1955, 1961; BALARIN, SCHENK). When mainly initial solution is excited, the miscibility gap shifts to smaller concentrations. On the contrary, when irradiation or other external action is applied to heterogeneous mixture of initial solid solution α and isolating surplus phase (solution or composition) γ, the latter's specific energy increases to a greater extent than that of the phase α; in this case miscibility gap shifts to greater concentration, i.e. solubility of the phase γ in the phase α increases.

When solid solution is subjected to spinodal decay the increase of its free energy by external action leads to the widening of concentration region where the solutions coexist; in this case metastable compound γ' may isolate.

Figures 1a and 1b schematically illustrate situations when as a result of irradiation and other external actions the free energy of phase 1 and correspondingly, phase 2 mainly increases; also shown is the growth of supersaturation versus composition in the cases considered.

As a result of non-uniformity of the excited state, a major local increase of specific free energy may stipulate a "trigger" mechanism facilitating the occurance of the centre of a new phase in microscopic volumes with increased thermodynamic supersaturation, since local supersaturation may exceed a threshold necessary for the nuclei of critical size to appear and thus stimulate the process of phase transition. On the other hand, local excitation of the forming nuclei of a new phase may lead to their dissolution.

V. Thermodynamic supersaturation with respect to stable and metastable phases

Simple substances and compounds which may be regarded as one-component ones, may exist not only in stable, lowest energy structural states, but also in several additional, higher excited metastable states.

Near absolute zero of temperature at normal pressure the minimum energy (ground) state corresponds to the highest energy of atomization H_{01}. All other metastable states have lower value of H_0:

$$|H_{01}| > |H_{0a1}| > ... > |H_{0an}| .$$

As a result of polymorphic transitions metastable phases (with respect to low-temperature phase) may become stable either at increased pressures or at sufficiently high temperatures, e.g. near the melting point, or even, in principle, at higher temperatures (overheating).

Taking into account this peculiarity of such metastable modifications, supposing that the difference of their free energies and that of a stable phase is small, we con-

a)   b)
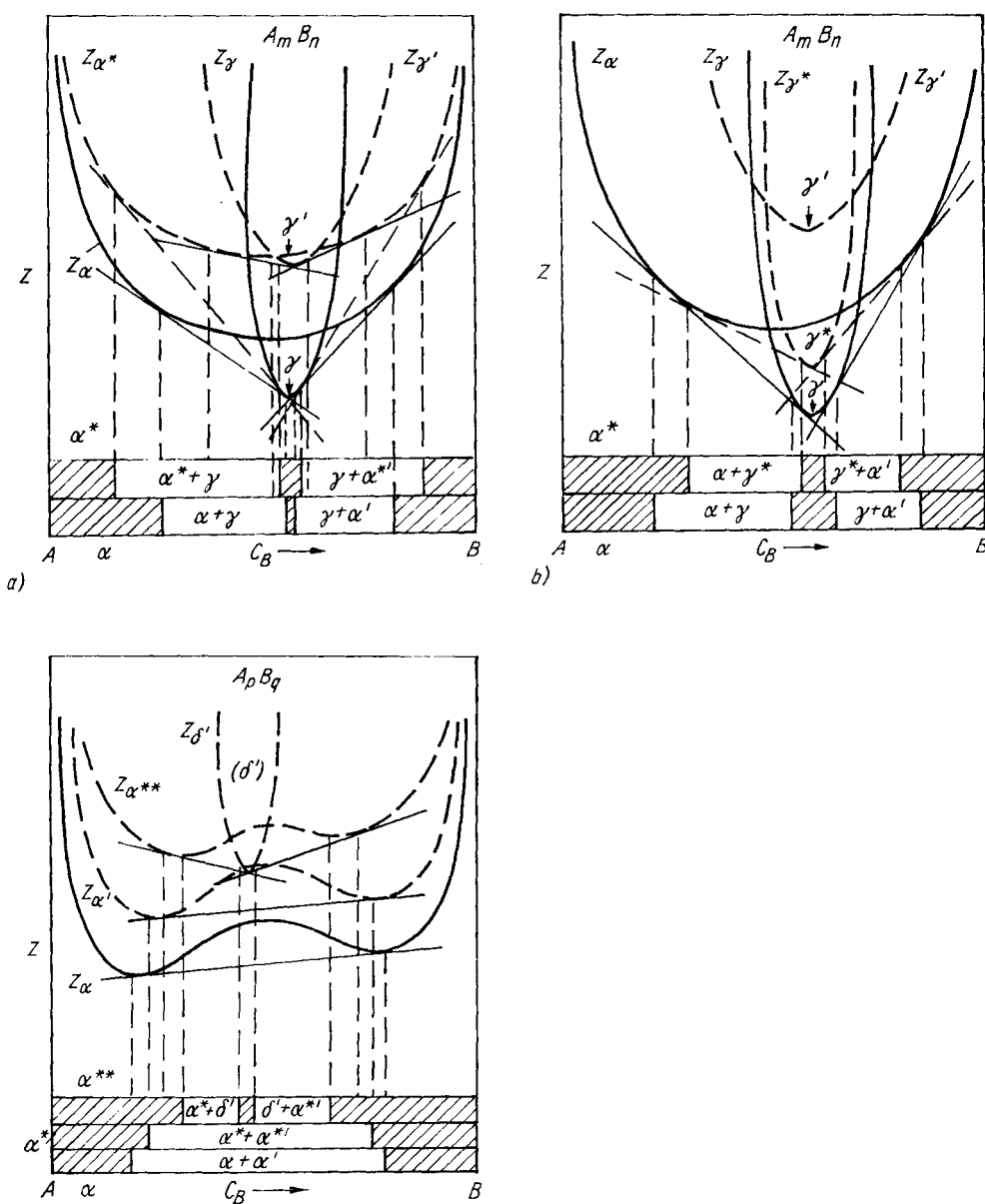
Fig. 1. Change of equilibrium conditions in binary system in case of excitation: a — of solid solution α, b — of stable compound $A_mB_n(\gamma)$, c — of solid solution subject to spinodal decay. Curves of Gibbs' free energy Z_α, Z_α^* refer to solid solution α, Z_γ, Z_γ^* — to compound A_mB_n in normal and excited states; Z_γ refers to metastable modification $A_mB_n(\alpha')$, Z_γ' — to metastable compound $A_pB_q(\delta')$

clude that to a first approximation the curves of $Z_{a1}, \dots Z_{an}$ versus temperature are practically parallel to the curve of the free energy Z_1 of equilibrium phase[4]).

In this case the value of thermodynamic supersaturation with respect to phase 2 at temperatures lower than T_k (which is the temperature of equilibrium transition of phase 1 into phase 2) will be determined by the magnitude of undercooling with respect to the temperatures $T_{a1}, \dots, T_{an}$, corresponding to the intersection points of the curves of the free energies of phases $a_1, \dots, a_n$ with that of the initial phase 2. Then

$$T_{an} = T_{k12} - \frac{H_{021} - H_{02an}}{S_2 - S_1}; \qquad T_{an} = T_{k12} \frac{\Delta H_{02an}}{\Delta H_{021}}.$$

The value of thermodynamic supersaturation of phase 2 with respect to the stable phase 1 and metastable phase a_n at temperature T may be evaluated by relation (see Fig. 2):

$$\Delta Z_{2an} = \Delta H_{021}(T_{2an} - T)/T_k ,$$

where ΔZ_{2an} is supersaturation with respect to metastable phase at; ΔZ_{21} is supersaturation with respect to stable phase 1, T is the temperature, lying lower than the
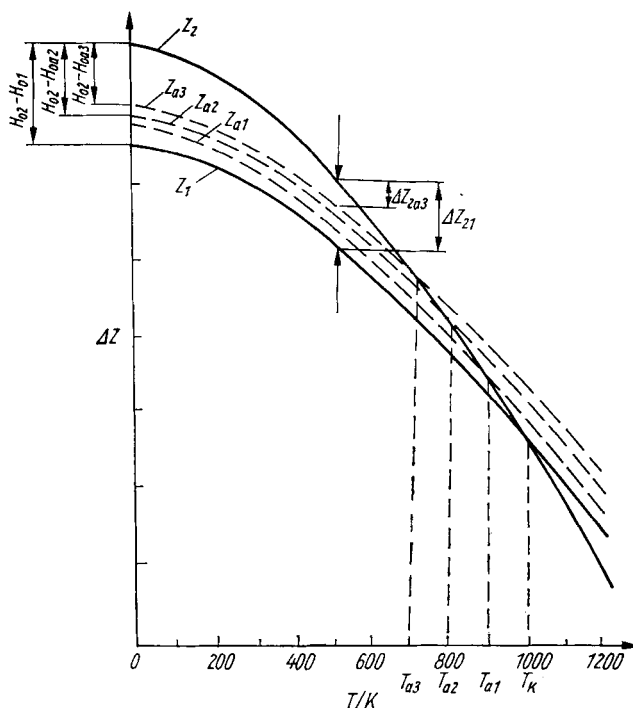
Fig. 2. Curves Gibbs free energy versus temperature for the phases: 2 (Z_2) and 1 (Z_1); metastable phases a_1 (Z_{a1}), a_2 (Z_{a2}), a_3 (Z_{a3})

---

[4]) In reality the decrease of atomization energy $|H_0|$ leads to the increment of entropy, i.e. rate of decrease of $-(\partial Z/\partial T)$ with the growth of temperature. The condition of parallelism of the curves may be adopted only as a first approximation when the deviations $H_{02} - H_{0an}$ of metastable phases atomization energy from that of a stable phase are small.

temperature of quasi-equilibrium transition from initial phase 2 to metastable phases *an*, so that

$$T_{an} < T_k; \qquad T < T_{an} .$$

When some generalized force X deviates from its equilibrium magnitude X_k, the values of thermodynamic supersaturation when the above suppositions are valid (i.e. Gibbs free energy of metastable phase is near that of phase 1 and both curves are parallel) are approximately as follows:

$$\Delta Z_{2an} = \Delta H_{021} \left(\frac{\Delta H_{02n}}{\Delta H_{021}} - \frac{T}{T_k} \right)$$

or

$$\Delta Z_{2an} = \Delta H_{21}(T_{an} - T)/T_k ,$$

adopting $\Delta H_{021} = \Delta H_{21}$.

Already this linear approximation in many cases appears to be sufficient for finding out of conditions and explanation of peculiarities of appearance of metastable phases in one-component systems depending on thermodynamic supersaturation.

VI. Work on appearance of nuclei of stable and metastable phases depending on thermodynamic supersaturation in one-component systems

For appearance and growth of nuclei of thermodynamically more stable phases than initial one, it is necessary that thermodynamic supersaturation ΔZ should exceed a certain critical value (GIBBS; VOLMER; VOLMER, WEBER; FARKASH; FRENKEL, 1939). The latter depends on the degree of stability of the phases, on energetic properties of initial and originating phases and, to a certain extent, on the transformation mechanism.

We proceed from the idea that whatever is the mechanism, the transformation has probabilistic character, each mechanism having its specific activation energy for transfer of atoms into positions corresponding to the centres of formation and growth of a new phase.

There are so-called homogeneous and heterogeneous crystallization processes. The first take place in absence of alien inclusions or substrates, the second in presence of them.

The idea that heterogeneous crystallization processes are those with ready centres of nucleation has a relative meaning. The formation of new phase nuclei on the bases or on the surfaces of inclusions is also a probabilistic process as in case of their spontaneous formation. There is a certain probability that a two-dimensional nucleus of new phase should appear and grow on the surface of a substrate or seed.

It is necessary to stress that in heterogeneous crystallization processes the value of thermodynamic supersaturation is considerably smaller than in homogeneous ones.

The effective activity of the substrate depends on microstructure of its surfaces, its crystallochemical affinity for the new phase, and on the other hand, on its macrostructure, i.e. presence of convex steps in the relief, cracks, recesses and pores (LEMLEIN; DANKOV; BLIZNAKOV; GORBUNOVA 1935, 1957; SIROTA 1962; FRENKEL; TEMKIN).

Let's remark that sometimes in recesses and pores the effective thermodynamic supersaturation required for the origination of new-phase nuclei is quite small or even zero (KAZACHKOVSKII; SIROTA 1962; TURNBULL 1950). Note also that new-phase growth on the surface of the base may take place via step dislocational mechanism (LEMLEIN; LEMLEIN, DUKOVA; FRANK, VAN DER MERVE; FRANK; FRANK, READ;

BURTON et al.; CHERNOV, A. A.) or via mechanism of "normal growth" (BARTENEV; REISS; BORISOV, DUKHIN; IVANTSOV, TILLER).

Adequate understanding of the mechanism of heterogeneous crystallization process in presence of bases and seeds, and condition of formation of metastable polymorphic modifications and phases is possible only on the basis of the principle of dimensional and orientational similarity of the crystal structure of initial and appearing phases and the base. This principle was elaborated by Dankov (DANKOV's principle), and then by BLIZNAKOV, ARKHAROV, TURNBULL and a.o.

In a wider sense it is necessary to take into account not only the crystallographic similarity of the phases taking part in the crystallization process, but also macro-structure of the base, wetting angles which has been shown already by VOLMER (1929), and the presence of near order in amorphous bases. (On the crystal-chemical nature of the phases see e.g. N. V. BELOV, BOKII, KREBS, KLEBER, ZHDANOV, PAUFLER and LENCHNER a.o.)

Numerous examples of crystallographic similarity of initial and appearing phases and a base were given by VOLMER and FLOOD, by BLIZNAKOV, KAISCHEW, MEHL, KURDJUMOV and SACHS, and by WASSERMANN.

As follows from above, relative thermodynamic supersaturation $\Delta Z/Z_k$ (relative undercooling $\Delta T/T_k$, relative pressure variations $\Delta p/p_k$ or $\Delta X_i/X_i$ when $T < T_k$, $p < p_k$, $X < X_k$) is the greatest with respect to the most stable phase and smallest with respect to the least stable of all phases, formation of which is thermodynamically possible under given conditions:

$$\frac{T_k - T}{T_k} > \frac{T_{a1} - T}{T_{a1}} > ... > \frac{T_{an} - T}{T_{an}}; \quad \frac{p_k - l}{p_k} > ... > \frac{p_{an} - p}{p_{an}};$$

$$\frac{X_{ik} - X_i}{X_{ik}} > ... > \frac{X_{ian} - X_i}{X_{ian}}.$$

Consideration of the shapes of free energy curves for initial and metastable phases illustrates that when supersaturation is small at $T_a < T < T_k$, and $p_a < p < p_k$ or in general $X_a < X < X_k$ only stable phase 1 is thermodynamically possible and formation of other phases is in principle prohibited,

Maximum work on appearance of nuclei (three-dimensional nuclei — centres of crystallization and two-dimensional nuclei addition of which conditions the rate of new phase growth) depends not only on the value of thermodynamic supersaturation ΔZ, but also on surface energy σ at the phase boundary, elastic deformation energy E_g caused by volume change[5]) and also work of other generalized forces related to the generalized coordinates $E_{xi} = \int X_i d(\Delta x_i)$. The change of Gibbs free energy $\Delta \Psi_3$ with the appearance of a three-dimensional nuclei with volume V_3 of new phase in thermodynamically supersaturated initial phase of one-component system is

$$\Delta \Psi_3 = - \frac{\Delta Z}{V} v_3 + \frac{v_3}{V} [E_g + E_{x} + E_{\mathcal{E}} + ... + T \Delta S_e] + K_{83} \sigma' v_3^{2/3} =$$

$$- \frac{\Delta Z'}{V} v_3 + K_{83} \sigma' v_3^{2/3}.$$

---

[5]) One of the first rather exact calculations of deformation energy in the process of formation of a new phase has been complied by MOTT and NABARRO, NABARRO (in aniso-tropic media see CAHN). The additional work resulting from volume change, electric and magnetic field change in the expressions for the work on appearance of nuclei and the rate of their formation — has been primarily accounted for by SIROTA (1945, 1946, 1948 c, d, 1957, 1961 a, b, 1962).

Here ΔZ is mole free energy difference for initial and appearing phases, $-\Delta Z' =$
$= -\Delta Z + \sum\limits_j E_j - T \Delta S_e$; ΔS_e is entropy change per mole as a result of new phase
formation, $\dfrac{1}{V} \sum E_j = \dfrac{1}{V} [E_g + E_{\mathscr{H}} + E_{\mathscr{E}}^+]$ is total energy change per unit volume as
a result of the change of the volume, electric, and magnetic field intensity, corre-
spondingly. K_{S3} is a form factor. In case of a sphere $K_{S3} = (36\pi)^{1/3}$, in case of a cube
$K_{S3} = 6$.

The equation $\dfrac{\partial \Psi_3}{\partial V_3} = 0$ gives the critical volume of a three-dimensional nucleus:

$$v_3 = (2/3 K_{S3})^3 \, \sigma'^3 / \Delta Z'^3 V^3 .$$

Reduced size of a three-dimensional nuclei of the cubic shape with a side a_3 is
$a_3 = \dfrac{4V\sigma'}{\Delta Z'}$ for a sphere $r_3 = \dfrac{2V\sigma'}{\Delta Z}$; if $\sum E_j = 0$ then $r_3 \cong \dfrac{2V\sigma'}{\Delta H} \dfrac{T_k}{\Delta T}$; because
$\Delta Z = \Delta H \, \Delta T / T_k$. Number of atoms (molecules) in the nucleus of critical size is then

$$n_3 = \frac{v_3}{v_A} = \left(\frac{2}{3} K_{S3}\right)^3 \left(\frac{\sigma'}{\Delta Z'}\right)^3 N^3 v_A^2$$

where v_A is the atomic (molecular) volume. For a spherical nucleus

$$n_3 = \frac{32}{3} \pi \frac{N^3 \sigma'^3 v_A^2}{\Delta Z'^3} ; \quad \text{if} \quad \sum E_j = 0 ,$$

then

$$n_3 = \frac{32}{3} \pi \frac{N^3 \sigma'^3 v_A^2}{\Delta H^3} \left(\frac{T_k}{\Delta T}\right)^3 .$$

Work on the formation of a critical-size nucleus is

$$A_3 = \frac{1}{2} \left(\frac{2}{3} K_{S3}\right)^3 \frac{\sigma'^3}{\Delta Z'^2} V^2 ;$$

if

$$\sum\limits_j E_j = 0 \quad \text{then} \quad A_3 = \frac{1}{2} \left(\frac{2}{3} K_{S3}\right)^3 V^2 \frac{\sigma'^3}{\Delta H^2} \left(\frac{T_k}{\Delta T}\right)^2 .$$

In case of as cubic nucleus

$$A_3 = 32 V^2 \sigma^{3'} / \Delta Z'^2 ;$$

if

$$\sum E_j = 0 \quad \text{then} \quad A_3 = 32 V^2 \frac{\sigma'^3}{\Delta H^2} \left(\frac{T_k}{\Delta T}\right)^2 .$$

Effective value of surface energy σ' depends on the size of a chip, a drop; e.g., ac-
cording to TOLMAN, and to KIRKWOOD and BUFF $\sigma' = \dfrac{\sigma_0}{1+2\sigma_0/r}$ or the smaller the
nuclei the stronger the dependence of the effective value of σ' on the size r. On the
other hand, σ' depends on elastic tensions and deformation of surface layers, and on
gradients of generalized forces.

Analogically to the idea of VOLMER, KOSSEL-STRANSKI-KAISCHEW of the crystal
growth mechanism by the addition of two-dimensional nucleus, the change of Gibbs

free energy in this process is

$$\Delta\Psi_2 = -\frac{\Delta Z}{V}\, v_2 + \frac{v_2}{V}\,[E_g + E_{\mathscr{H}} + E_{\mathscr{E}} + \ldots - T\,\Delta S_e] = -\frac{\Delta Z'}{V}\, v_2 + K_{S2}\varkappa v_2^{1/2}$$

where K_{S2} is a form factor of two-dimensional nucleus. In case of a disc (of thickness δ) $K_{S2} = 2\sqrt{\pi/\delta}$; in case of square prism $K_{S2} = 4/\sqrt{\delta}$; $\varkappa$ is peripheral energy.

From the equation $\dfrac{\partial\Psi_2}{\partial v_2} = 0$ critical volume of a two-dimensional nucleus may be found:

$$v_2 = \left(\frac{K_{S2}\varkappa V}{2\Delta Z'}\right)^2 ; \quad \text{if} \quad \sum_j E_j = 0 \quad \text{then} \quad v_2 = \left[\frac{K_{S2}V^{\mathscr{H}}}{\Delta H}\,\frac{T_k}{\Delta T}\right]^2 .$$

The side of a square nucleus of critical size a_2 is

$$a_2 = \frac{2V\varkappa}{\Delta Z'\delta} = \frac{2V\sigma}{\Delta Z'} ; \quad \text{if} \quad \sum E_j = 0 \quad \text{then} \quad a_2 = \frac{2V\sigma}{\Delta H}\,\frac{T_k}{\Delta T}.$$

Radius of the disc nucleus is $r_2 = \dfrac{V\varkappa}{\Delta Z'\delta} = V\sigma/\Delta Z'$;

if

$$\sum_j E_j = 0 \quad \text{then} \quad r_2 = \frac{V\sigma}{\Delta H}\,\frac{T_k}{\Delta T}.$$

Here peripheral energy $\varkappa$ is proportional to the surface energy, $\varkappa \cong \delta\sigma \cong d\sigma$ (here d is interplane distance), according to STRANSKI and KAISCHEV. The work on formation of two-dimensional nucleus of a critical size is $A_2 = \left(\dfrac{K_{S2}}{2}\right)^2 \dfrac{V\varkappa^2}{\Delta Z'}$; so for a square nucleus $A_2 = \dfrac{4V\varkappa^2}{\Delta Z'\delta}$; for a disc nucleus $A_2 = \dfrac{\pi V\varkappa^2}{\Delta Z'\delta}$.

A. Work on formation of three-dimensional nuclei depending on thermo-dynamical supersaturation caused by the temperature change

Let us consider the temperature dependence of the work on nuclei formation. We adopt a number of simplifying assumptions: i) absence of external fields and stresses at the phase boundaries of one-component substance, $\sum_j E_j = 0$; ii) proportionality of surface energy at the phase boundaries to specific energy of phase transition, $\sigma = \beta\,\Delta H$. (The question of proportionality of surface energy at $T = 0$ to atomization heat and to melting-heat follows from the analyses of STRANSKI and KAISCHEW, of SIROTA (1943, 1962 a, b) and has been discussed in detail by SKAPSKI, ORIANI, SEMENCHENKO, 1957 a) (SIROTA (1943, 1962); TURNBULL and HOLLOMAN, and by TURNBULL 1950). We assume, as it is usually adopted that $\Delta Z = \Delta H\,(\Delta T/T_k)$. In this case the size of a three-dimensional spherical nucleus is $r_3 = 2V\beta\,(T_k/\Delta T)$ and the work on the formation of a three-dimensional nucleus of a new phase in the units of kT as a function of relative undercooling is (SIROTA 1948 b, d)

$$A_3/(kT) = \gamma_3\,\frac{\Delta H}{kT}\left(\frac{T_k}{\Delta T}\right)^2 .$$

Similarly the work on formation of a three-dimensional nucleus as a function of relative change of any generalized force X is

$$A_3/(kT) \cong \gamma_{3i}\,\frac{\Delta H}{kT}\left(\frac{X_{ik}}{\Delta X_i}\right)^2 .$$

B. Work on formation of two-dimensional nuclei as a function of relative undercolling and deviation of a generalized force from its equilibrium value

At analogous basis the work on formation of a two-dimensional nucleus as a function of relative undercooling supposing that the role of other factors is small, is

$$A_2/(kT) = \gamma_2 \frac{\Delta H}{kT} \frac{T_k}{\Delta T} \ .$$

The work on formation of two-dimensional nucleus as a function of relative deviation of any generalized force from equilibrium value is

$$A_2/(kT) = \gamma_{2i} \frac{\Delta H}{kT} \frac{X_{ik}}{\Delta X_i} \ .$$

Here γ_3, γ_{2i}, γ_2, γ_{2i} are proportionality quotients.

C. Work on formation of metastable-phase nuclei in case of undercooling

Analysis of the shapes of the plots of the work on formation of three- and two-dimensional nuclei of a stable phase 2 and metastable phases 2^a, 3^a, ... versus undercooling testifies that under adopted conditions the smallest work in the units of kT corresponds to the stablest phase 1 and the greatest work — to the least stable phase "a", if undercooling (or supersaturation) is small. At temperature lower than $1/3\ T_k$ for three-dimensional nuclei and lower than $1/3\ T_k$ for two-dimensional nuclei this relation reverses: the smallest work on the formation of three- and two-dimensional nuclei corresponds to the least stable phase "a".

Free energy curves for stable 1, 2 and metastable a_1, a_2, a_3 modifications of one-component system are shown in Figure 2.

The curves of the work on formation of three-dimensional (A_3/kT) and two-dimensional (A_2/kT) nuclei versus temperature are presented in Figure 3. In the process of computation the following values of the quantities have been assumed:

$\Delta H_{21} = 1.43$ kcal/mole;	$T_{k1} = 1000$ K
$\Delta H_{2a1} = 1.25$ kcal/mole;	$T_{a1} = 900$ K
$\Delta H_{2a2} = 1.10$ kcal/mole;	$T_{a2} = 800$ K
$\Delta H_{2a3} = 0.95$ kcal/mole;	$T_{a3} = 700$ K
$U = 14.3$ kcal/mole	$\gamma_3 = 2.$

As may be seen from the given Figure 3 when undercooling (or thermodynamic supersaturation) is small, most probable is appearance and growth of the stable phase nucleus. When supersaturation is great it is most probable that the least stable, furthest from equilibrium metastable phase will form and grow, since the work on its formation is the smallest.

It also follows from the carried-out analysis that Ostwald's step rule in its general form may be valid for one-component systems in case of sufficiently large supersaturation.

Elastic stresses arising as a result of the difference of specific volumes of initial and appearing phases or caused by imperfect conjugation of crystallochemical lattice of orginating phase with a base (or a seed) may to a certain extent change this relation in the intermediate domain of supersaturation, facilitating the formation of a phase with maximum crystallochemical affinity or crystallographic conformity with initial phase (or seed). However, the above conclusion remains valid in its general
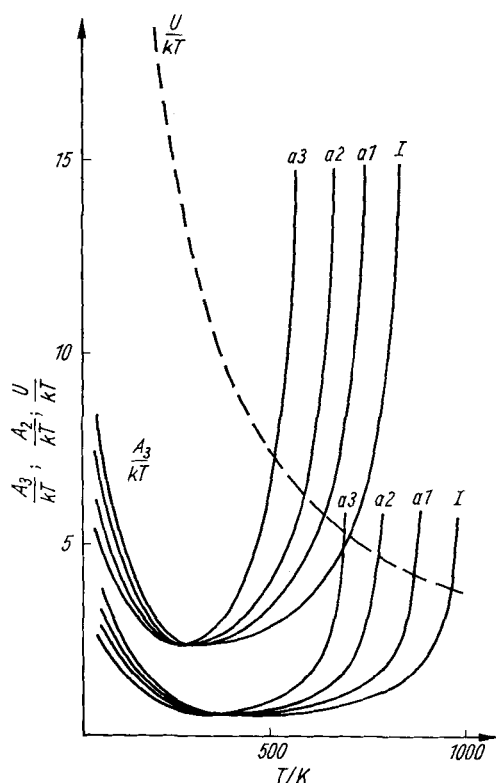
Fig. 3. Work on formation of three- and two-dimensional nuclei in the units of kT: A_3/kT and A_2/kT versus temperature for stable phase 1 and metastable phases a_1, a_2, a_3. Also shown is activation energy U/kT ($U = 14.2$ kcal/mole) Computation

form: in case of small thermodynamical supersaturation the smallest work on formation of nuclei corresponds to most stable phase and on the contrary in case of major thermodynamic supersaturation the smallest nucleation work corresponds to the farthest from equilibrium, least stable phase. In the range of intermediate supersaturations the substantial role is played by crystallochemical and crystallographic relations of appearing phases with initial phase or seed.

VII. Main factors causing polymorphic phase transition (crystallization)

Sufficiently complete physical substantiation of Ostwald's step rule and determination of its applicability limits is possible on the basis of detailed study of kinetics of the phase transformation (crystallization) of initial phase 2 into stable (under given conditions) phase 1 or metastable phases $a_1, a_2, \ldots, a_n$.

It is well-known (D. K. CHERNOV, 1868, 1898; TAMMANN 1903) that every phase transformation process takes place by means of formation of nuclei-"germs" of the new phase — the centres of crystallization and of their growth. VOLMER-type process of growth via two-dimensional nucleation is not the only possible one. Other feasible processes are: the growth on dislocations, prominences; branchy (dendritic, needle-shaped), martensite growth, and also so-called "normal growth". The example of

normal growth is the growth of fluid drops in supersaturated vapour: here there are no two-dimensional nuclei.

The difference of absolute values of linear rate of VOLMER growth via addition of 2-dimensional nuclei and that of normal growth in principle cannot be great, at least in the region of moderate undercooling (supersaturation). A low undercooling VOLMER growth rate exceeds the rate of normal growth. At great undercooling, conversely, the VOLMER growth rate may become lower than that of normal dislocational, dendritic growth, Widmanstette-type and naturally, martensite-type growth.

First order phase transitions are in principle fluctuational ones. Fluctuational character of transformation is revealed in the case of spontaneous occurance and growth of nuclei of new phase in initial one as well as in presence of seeds and bases where the germs of the new phase come to existence and growth. The rate of the transformation processes is determined by the rate of the formation of new phase nuclei, and depends finally on the magnitude of "moving force" — thermodynamic supersaturation, mobility of atoms — and, on the other hand, on the "resistance force" — the amount of work on the formation of new phase centres and on the movement of atomic layers in the process of their growth.

In crystallization or recrystallization process together with well-known factors (i.e. value of thermodynamic supersaturation, existence of shape and orientational correspondence, crystallochemical affinity) a significant role is played by various unaccounted factors stipulated by the existence of short-range order, "microheterogeneity", initial thermodynamically supersaturated phase, and its change with the growth of the supersaturation. Major influence upon the peculiarities of the transformation kinetics is exerted by the change of transformation mechanism and related change of activation energy. At similar circumstances KURDYUMOV (1930, 1949, 1952, 1960) analysed processes of martensite transition.

For example, with the increase of thermodynamic supersaturation (undercooling) three-dimensional nucleation sometimes gives place to branchy dendritic, Widmann-stätten-type growth, trostomartensite and then to martensite-type transition mechanism. The shape of growing crystallites exerts substantial influence on the regularities of time development of the transformation process, including isothermal process, and on its temperature dependence.[6])

In undercooled fluids, like any other thermodynamically supersaturated phase, the formation of various quasi-stable "pre-nuclei" of new phase with different structures is taking place, their size and stability being comparable to, or even exceeding those of growing stable and metastable phase nuclei (SIROTA 1961).

In processes of phase transformation the role of suspension of such associations or complexes is rather considerable. Presence of this "plankton" (expression of A. A. BAJKOV) may modify or even determine the flow of transformation process, may cause preferential formation of a certain metastable, thermodynamically possible phase.

In a number of cases the formation of new-phase nuclei may take place via coalescence of pre-nuclei and their recrystallization. Formation of relatively stable short-range complexes and quasistable pre-nuclei in the initial phase may be conditioned by a number of processes. Among them are the following ones. In thermodynamically supersaturated transitional phases a new "quasi-phase" may sometimes originate from the closest packing of ions with space-type, instead of surface-type structure (Fig. 4). They may form via addition of ions to tetrahedric holes formed by three adjacent ions lying on the surface of the complex or pre-nucleus (SIROTA 1961a, 1967;

---

[6]) The dependence of the shape of growing crystals on undercooling had been analysed by ARTEMJEV, DAVENPORT and BAIN, MEHL and SMITH, FRIDLANDER (1948) et al.
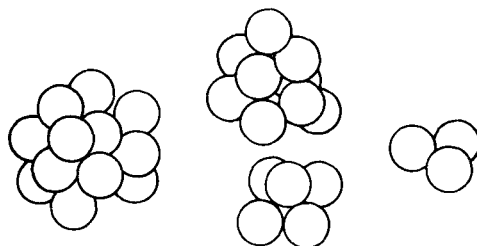
Fig. 4. Clusters forming via space dense packing containing 3, 5, 11, 17 atoms

SHTERENBERG). Existence of quasi-stable pre-nuclei of several critical sizes with various types of structure may be explained also by a certain dependence of surface energy on the size of new-phase pre-nuclei, by difference of specific volumes and correspondingly by difference of deformation field energy in the vicinity of appearing pre-nuclei, etc. Also processes of internal composition redistribution, internal adsorption (ARKHAROV), presence of Cottrell's atmosphere may exert major influence.

The role of these and other factors influencing the sequence of phase formation has not been cleared yet despite the significance of the question.

Later we shall confine ourselves to the qualitative consideration of metastable phase formation conditions in VOLMER-type processes — three-dimensional nucleation and subsequent growth of new phase nuclei within the initial phase. However, one must keep in mind that non-VOLMER-type processes described above may exert decisive influence upon the flow of transformation processes and the sequence of appearance of metastable phases (polymorphic modifications).

In order to analyse the succession and kinetics of the isolation of stable and metastable phases from thermodynamically supersaturated initial phase we shall briefly consider elementary processes of first-order phase transition, using classical ideas of GIBBS-VOLMER, VOLMER (1939), FARKASH, BECKER and DÖRING, STRANSKI and KAISCHEW, Ja. I. FRENKEL (1941, 1945), Ja. B. ZELDOVICH, SEMENCHENKO and PETROVSKII and the methods developed by the author (SIROTA 1945, 1948, 1957, 1962a, b), see also DANILOV; KUZNETSOV (1937, 1963), DUNNING.

The rate of formation of three-dimensional nuclei in the volume V of a mole of initial phase may be semi-quantitatively represented as a product of a number of factors: W_3'' — the probability of successive transformation into a nucleus of a new phase of an activated group of n_3 atoms having the critical volume; W_{3c} — the probability of concentration fluctuation in the result of which the composition of this group of atoms will correspond to the composition of appearing phase; P_3 — survival probability for the forming nucleus, N_D/n_3 — number of groups containing n_3 atoms each among N_D moving activated atoms in the volume V of a mole of initial phase in a unit time;

$$W_3 = \frac{N_D}{n_3} W_3'' \cdot W_{3c} P_3 ,$$

where[7])

$$N_D = N \nu e^{-U/kT} .$$

Here ν is the effective frequency of atom oscillations. The probability P_3 of survival of a three-dimensional nucleus will in its turn be determined by the product of the

---

[7]) TURNBULL and FISCHER 1949 (see also HOLLOMAN and TURNBULL 1953) using the method of absolute reaction rates, included kT/h into pre-exponential factor, instead of ν in present work, since it may be adopted that $h\nu = kT$. However it may be more convenient to use characteristic temperature θ substituting ν by $(k/h) \theta$.

probability W_2'' of the group of n_2 atoms, a progenitor of a two-dimensional nuclei, to occur on the surface of a three-dimensional nucleus, by the ratio F_3/F_2 of the surfaces of three- and two-dimensional nuclei, by the probability W_{2c} of the composition of this two-dimensional nucleus to correspond the composition of the new phase, by the probability $W_{2\eta}$ of proper orientation of atom or a group of atoms with respect to the surface to which they adjoin, by the probability P_2 for this nucleus to continue its growth, but not to dissolve, $P_2 \cong W_{02} \cong 1/2$. Thus,

$$W_3 \cong \frac{N_D}{n_3}\, W_3'' W_2'' W_{3c}' W_{2c} W_{2\eta} W_{02}(F_3/F_2)\,.$$

Similarly the probability of the appearance of a two-dimensional nucleus on a unit surface of a growing crystal in a unit time will be determined by a product of a probability W_2'' for the activated group of n_2 atoms to transform into a two-dimensional nucleus, by the probability W_{2c} of a concentration fluctuation in the volume of a two-dimensional nucleus from activated composition of initial phase to the composition of a new phase, by the probability $W_{2\eta}$ of proper orientation of the adding atom (or particle), by the number N_{2D}/n_2 of groups of n_2 atoms each among N_{2D} atoms, which is the difference of the number of atoms striking the unit surface of a growing crystal and the number of reflected atoms, by the probability P_2 for the nuclei not to dissolve

$$W_2 \cong (N_{2D}/n_2)\, W_2'' \cdot W_{2c} \cdot W_{2\eta} \cdot P_2\,.$$

Linear growth rate c of a crystal to a first approximation may be adopted as $c \cong \cong W_2\delta$. (δ is thickness of two-dimensional nucleus.)

In accordance with Boltzmann's statistics it is assumed that

$$W_3'' \cong e^{-A_3/kT}\,, \qquad W_2'' \cong e^{-A_2/kT}\,,$$

where A_3 and A_2 are respectively the works on the formation of three- and two-dimensional nuclei of critical volume.

Resulting functional dependence on ΔT of probabilities of appearance of three- and two-dimensional nuclei (concentration fluctuations are disregarded) is as follows:

$$W_3 \cong K'(\Delta T/T)^3\, e^{-K_1/T} \cdot e^{-K_2/T(T_k/\Delta T) - K_3/T(T_k/T)^2} \cdot e\,,$$

$$W_2 \cong K''(\Delta T/T)^2\, e^{-K_1/T} \cdot e^{-K_2/T(T_k/\Delta T)}\,.$$

The work involved in the fluctuation of the nucleus composition leading from initial to new phase is in case of two-dimensional nuclei kTB_2n_2 and in case of three-dimensional nuclei kTB_3n_3 where

$$B_2 \cong (C-\alpha)^2/(2C_1\alpha_2)\,, \qquad B_2 \cong B_3\,.$$

Using Gauss distribution we obtain the probability of the concentration fluctuation in the binary solution of phase 1 from active composition α_2 to C_1, corresponding to the composition of new phase;

$$W_{3c} \cong \eta_3\, e^{-\frac{(C_1-\alpha_2)^2 n_3}{2C_1\alpha_2}}\,; \qquad W_{2c} \cong \eta_2\, e^{-\frac{(C_1-\alpha_2)^2 n_2}{2C_1\alpha_2}}\,,$$

where

$$\eta \cong \frac{1}{\sqrt{2\pi C_1(1-C_1)}}\,, \qquad \eta_2 \cong \eta_3 \cong \eta\,.$$

Calculation of concentration fluctuation probability can be compiled with the help of different methods: statistical thermodynamics, Smoluchowski's statistical method which has been used by e.g. Stark et al. Fink and Smith used Poisson distribution

in computation of fluctuation probability. In our work we used Gauss distribution (see e.g. GNEDENKO, GLIVENKO).

Analysing the formation rate of the three-dimensional nuclei W_3, linear growth rate of nuclei and massive crystals $C \cong W_2\delta$ we must take into account the size of three-dimensional crystals, the growth rate of the two-dimensional nucleus along the growing face of a crystal, the dependence of surface energy on the size of chips and other factors, among them the size of the activity volumes in which the processes named take place in proper time.

It is assumed that the two-dimensional nucleus increases rapidly along the growing face of the crystal within the active region considered, the appearance of the new layer being caused by addition of one two-dimensional nucleus. It is assumed therefore that probability of formation of two-dimensional nucleus is related to the probability of origination of a new layer on the growing surface of the crystal. This may be true if growing crystals are relatively small and supercooling is also small.

In the analysis of the succession of formation (crystallization) of stable and metastable phases to the first approximation the dependence of the surface energy on the dimensions of the chips is not as a rule taken into account.

Let's remark that ultimately the linear growth rate C is determined by the difference of fluxes Φ_2 and Φ_1 of particles (atoms, ions or molecules) moving off the initial phase and off growing new phase, correspondingly, normally to the growing surface of the crystal, $C \cong K_d(\Phi_2 - \Phi_1) \cong Z_2\xi_2 - Z_1\xi_1$. The fluxes Φ_2 and Φ_1 are referred to a unit surface in a unit time; K_d is a coefficient including geometric and accomodation factors; ξ_1 and ξ_2 are kinetic coefficients depending on activation energy, structure of phase boundary and process mechanism. In thermodynamic equilibrium $\Phi_1 = \Phi_2$, $C = 0$. In case of thermodynamic supersaturation $\Phi_1 < \Phi_2$. The flux off initial to growing phase Φ_2 is in general greater than the flux Φ_1^0 conditioned only by its free energy per unit volume (Z_1/V): $\Phi_1 \cong \Phi_1^0\zeta, \zeta > 1$. This is due to peculiarities of surface structure caused by the transformation mechanism, to number of growth points, i.e. because of factors usually called "kinetic", which are in fact connected with local changes of surface energy.

Time evolution of the isothermal transformation of initial phase with sufficient accuracy is described by KOLMOGOROV-type expression see also KAZEYEV (1936, 1956), AVRAMI (1939), JOHANSON and MEHL, SIROTA (1942, 1950). This problem has been considered also by GÖLLER and SACHS; TAMMANN; LIPILIN; RODIGIN, etc., see ZHDANOV; BELENKII.

In the form given by SIROTA (1942, 1953) the expression describing kinetics of isothermal transformation process is as follows:

$$V_\tau = V_0 \left\{ 1 - \exp\left[-\left(\frac{1-\nu}{2-\nu}\right)^{\frac{2-\nu}{1-\nu}} \cdot A^{\frac{1}{1-\nu}} \cdot \tau^{\frac{2-\nu}{1-\nu}} \right] + \dots + v_3^* \tau \right\},$$

where $A = K_s C_1$, $\nu = \frac{2}{3}$ for three-dimensional growth, $\nu = \frac{1}{3}$ for two-dimensional growth; $\nu = 0$ for one-dimensional growth; v_3^* is volume of a new phase centre which practically cannot grow, e.g. martensite "needle".

In the case of three-dimensional growth, according to KOLMOGOROV, by the moment τ the volume of transformed phase V_τ in the initial volume V_0 is $V_\tau = V_0(1 - e^{-1/3\pi W_3 C^3 \tau^4})$ KOLMOGOROV's formula and the analogous formula by JOHANSON and MEHL for finite volumes of initial phase are approximate though the main part of the process is described with good accuracy. If the linear growth rate if $C \cong W_2\delta$ and m is the fraction of the transformed phase, $m = V_\tau/V_0$, by the moment τ_m we have

$$\ln \tau_m = \tfrac{1}{4} \left\{ \ln[\ln (1 - m)] - \ln \pi/3 - \ln W_3 - 3 \ln W_2 - 3 \ln \delta \right\}.$$

Earlier we remarked (Sirota 1950) that these expressions were not exact, in particular for complete transformation time ($m \to 1$, $\tau \to \infty$) because in finite volumes which are parts of any initial volume and contain one or more growing nuclei appearing in initial finite time interval, the total transformation time cannot exceed $\tau_m = R/C_{\min}$, where R is the radius of the sphere enclosing the volume of initial phase, and $C_{\min} \cong$ $\cong (W_2\delta)_{\min}$ the linear rate of isothermal growth of the nucleus, which appeared in the initial moment ($\tau = 0$).

Kinetics of isothermal processes of eutectic or eutectoid transformations, despite a series of specific peculiarities (presence of leading phase, special role of diffision; see Bochvar, Bochvar and Tamman, Bochvar and Gorev; Cahn) is formally described by the same equations.

VIII. Influence of thermodynamic supersaturation and of relative undercooling value upon the kinetics of formation of stable and metastable phases in one-component systems

Analysis of the given equation which explains experimental data comparatively well, permits to obtain a number of conclusions. Firstly, time τ_m of isothermal transformation of m-th fraction of initial volume, described by this equation, descreases with the growth of thermodynamic supersaturation at a given constant temperature.

Secondly, when supersaturated phase 2 transforms not only into stable phase 1 but also into metastable phases $a_1, \ldots, a_n$, the time of transition into metastable phases shortens with the growth of phase 2 supersaturation with respect to each of them. Note that if $\Delta Z_i \to 0$ then for corresponding phase i $\ln \tau_{mi} \to \infty$.

Thirdly, if supersaturation (undercooling) is small, the stable phase has the smallest value of $\ln \tau_{mi}$. Conversely, if supersaturation (undercooling) is greater than a certain value ΔZ_μ the transition time will be the shortest for the least stable phase.

As it was remarked above, the surface energy σ_i on the boundary between initial and appearing phase i is approximately proportional to the energy of phase transition $\sigma_i \cong \beta \Delta H$. Consequently surface energy on the boundary initial phase — stable phase 1 is greater than on the boundaries initial phase — metastable phase, $\sigma_{21} >$ $> \sigma_{2a1} > \ldots > \sigma_{2an}$, according to the relation $|\Delta H_{21}| > |\Delta H_{2a1}| > \ldots > |\Delta H_{2an}|$.

Time of transformation of a certain m-th fraction of initial phase into stable phase 1 with increasing supersaturation ΔZ_{21}, decreases slower than that of metastable phases $a_1, \ldots, a_n$. As a result of this there appear intersection points on the curves $\ln \tau_{m1}$, $\ln \tau_{ma1}, \ldots$, $\ln \tau_{man}$.

In case of major supersaturation values, exceeding ΔZ_μ: $\Delta Z > \Delta Z_\mu$ the greatest rate and, consequently, the shortest time of transformation corresponds to the formation of the least stable phase a_n.

When temperature falls lower than T_k thermodynamic supersaturation grows and the work on formation of three- and two-dimensional nuclei A_3/kT, A_2/kT passes through minimum. At the same time the mobility of atoms which depends on activation energy U, decreases exponentially.

Consequently time logarithm $\ln \tau_m$ for isothermal transition of m-th fraction of initial phase has a minimum at a certain undercooling.

In particular, when thermodynamic supersaturation is due only to undercooling, $\Delta Z = \Delta H (\Delta T/T_k)$ then, as follows from Gibbs-Volmer-Frenkel' theory, the work on formation of three-dimensional nuclei A_3/kT has its minimum at $T = T_k/3$ and that for two-dimensional nuclei A_2/kT at $T = T_k/2$ and respectively time logarithm $\ln \tau_m$ will be practically near its minimum (which is given by the equation $\partial \ln \tau_m/\partial T = 0$).
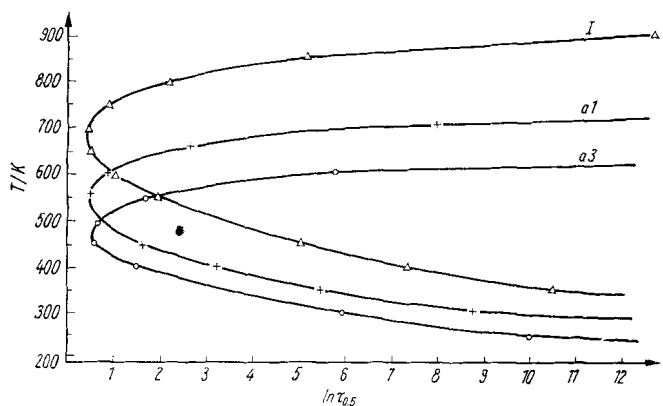
Fig. 5. Time logarithm for half-transformation of initial phase 2 into stable phase 1 ($T_k =$ $= 1000$ K, $U = 18$ kcal/mole and into its metastable modifications ($T_k = 800$ K, $U = 14.2$ kcal/ mole; $T_k = 700$ K, $U = 12$ kcal/mole). Computation $\tau(s)$

As can be seen from Figure 5, only for undercooling to the temperature lower than 500 K, the shortest transformation time $\tau_{0.5}$ ($m = 0.5$) corresponds to the least stable phase a_3, i.e. in the first instant the farthest from equilibrium phase will isolate in accordance with Ostwald's step rule. (See also Fig. 6.)

Consequently Ostwald's step rule in the case considered is valid only when supersaturation is large.
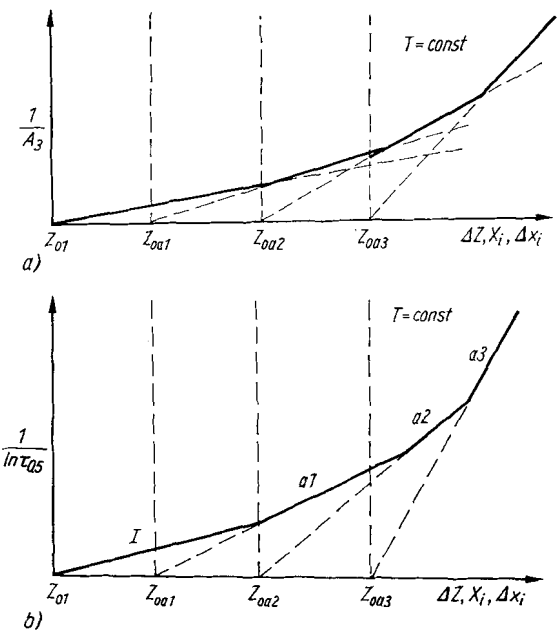

Fig. 6. Regions of thermodynamic supersaturation ΔZ, corresponding to a) the minimum nucleation work A_3 b) minimum time logarithm $\ln \tau_{0.5}$ for half-transformation of initial phase 2 into stable 1 and metastable modifications a_1, a_2, a_3. A scheme

Here an important role is played by the diffusive mobility of atoms, which decreases exponentially as temperature falls.

Effective diffusion activation energy U is different in case of formation and growth of stable and metastable phases. If we adopt that diffusion activation energy is proportional to the temperature of equilibrium or quasi-equilibrium transition $U_i \cong aT_{ci}$ (e.g., according to Bugakov, diffusion activation energy U_D in crystals is related to the melting temperature T_s: $U_D \cong 20T_s$), then the complicated character of C-shape stability curves is clearly revealed and correspondingly the sequence of appearance of metastable phases at great supersaturations is clearer.

However, the question on the dependence of activation energy of the transformation process on the transition temperature has to be elucidated. Possibly this dependence is due mainly to the difference in mechanisms of transition into stable and metastable phases. Diffusion activationenergy of initial phase, as a rule, grows when temperature lowers. Therefore decrease of activation energy in case of formation of metastable phases with lower transition temperatures may result from additional factors, among them being: composition change of forming phases and, which is more important, difference in transition mechanisms (Kurdyumov), due to autocatalysis (Dehlinger 1939; Sirota 1955, 1967), elastic deformations caused by volume change in transformation (Nabarro, Cahn, Darken and Gurry) a.o.

The basis of diffusion theory of growth of a needle of new phase has been laid by Ivantsov (see also Hillert).

IX. Influence of the change of pressure and other generalized forces upon the sequence of formation of stable and metastable phases

When pressure is changed isothermally, with the growth of relative pressure deviation from the equilibrium value P_k, i.e. with the growth of thermodynamic supersaturation the transformation time logarithm decreases. If the formation of phases 1, a_1, ... , a_n out of supersaturated with respect to them phase 2 is thermodynamically possible, when $p < p_a < p_{a1} < p_{21}$ the resulting curve $\ln \tau_m$ has a complicated character. If $p < p_\mu$ the smallest transformation time refers to the formation of the least stable phase a_n. When relative deviation of pressure from P_k is small, the stable phase is the first to isolate.

Similar regularities concerning succession of formation of stable and metastable phases out of thermodynamically supersaturated phase 2 in isothermal conditions take place when any of generalized forces X_i deviates from its equilibrium value X_{ik} causing the growth of thermodynamic supersaturation ΔZ (Fig. 6).

The dependence on ΔZ of work on formation of nuclei of stable and metastable phases and of half-transformation time (of transition of initial phase into stable and metastable phases) other things being equal will be determined by the surface energy σ_{2i} on the interfaces of initial phase with stable and metastable phases.

Influence of pressure and other generalized forces upon self-diffusion coefficient may change the shape of the curves $\ln \tau_m$ vs $\Delta p/p_k$ but practically does not change the above regularities with respect to succession of formation of stable and metastable phases, at least in the regions of small and great thermodynamic supersaturation.

Analysis of the results obtained shows that in case of small thermodynamic supersaturations resulting from deviation of pressure or any other generalized force from its equilibrium value, the most stable phase isolates in the first instance.

Conversely, in case of major thermodynamic supersaturations it is the least stable phase that appears the first. Consequently under considered conditions of pressure

(or any other generalized force) change, Ostwald's step rule is valid also when deviation of pressure (or generalized force) from its equilibrium value is great.

As regards the sequence of formation of metastable phases a special role is played by the pressure change occuring in the transformation process because of the difference of specific volumes and elastic properties of initial and forming phases.

When new phase has a greater specific volume than the initial one, the pressure is growing causing slowing of the transformation process. A transition which takes place on the external surface of initial phase in vacuum and which is non-variant first-order phase transition, may adopt a character of polyvariant second-order transition within the volume of initial phase as a consequence of the pressure change. Significant hysteresis is exercised when the external factor (temperature, pressure) variation direction is reversed.

When thermodynamic supersaturation is sufficient, the probability of formation and growth of metastable phase nuclei with the smallest specific volume may be the greatest, and correspondingly, its separation will be preferencial, at least in the region of moderate thermodynamic supersaturation.

X. Influence of crystal bases and seeds upon the rate and succession of isolation of redundant stable and metastable phases

In presence of seeds and bases with sufficient dimensional and orientational correspondance and hence crystallochemical affinity with appearing phase (DANKOV), the work on formation of a nucleus upon the base is approximately equal to the work on formation of two-dimensional nucleus and is in any case essentially smaller than that for three-dimensional nucleus in the absence of seeds.

In the case of complete crystallographic and crystallochemical correspondence transformation time logarithm for m-th fraction of initial phase is given by expression:

$$\ln \tau_m = B_m - \frac{U - \frac{4}{3}A_2 + \frac{1}{4}n_2^3 - B_2}{kT}.$$

Here we neglect fluctuations of concentration and deformation energy. As may be concluded from the above formula, the transformation time in the case considered is mainly determined by the work on formation of a two-dimensional nucleus. When composition of appearing phase differs from that of the initial one we must take into account the concentration fluctuation probability in its volume.

If the crystallochemical affinity of the base for one of the metastable phases takes place, nevertheless, if thermodynamic supersaturation is small or if formation of metastable phase is thermodynamically impossible, in the first instant only stable phase will form. In case of somewhat larger values of thermodynamic supersaturation the mentioned metastable phase, having crystallochemical affinity for the bases, will predominantly form upon the base.

However, even in the presence of bases at relatively large supersaturation most probably there will first appear the least stable phase out of all thermodynamically possible phases.

In Figure 7 are shown C-shape curves for the transition of phase 2 into phase 1 without bases and seeds and for transition of phase 2 into a metastable phase "a" in the presence of inclusions having crystallochemical affinity for the appearing metastable phase. As may be seen the resulting curve has a complicated shape, at temperature higher than T_μ stable phase predominantly forming, and at $T < T_\mu$ — metastable phase at, the most distant from equilibrium, forming. If crystallographic
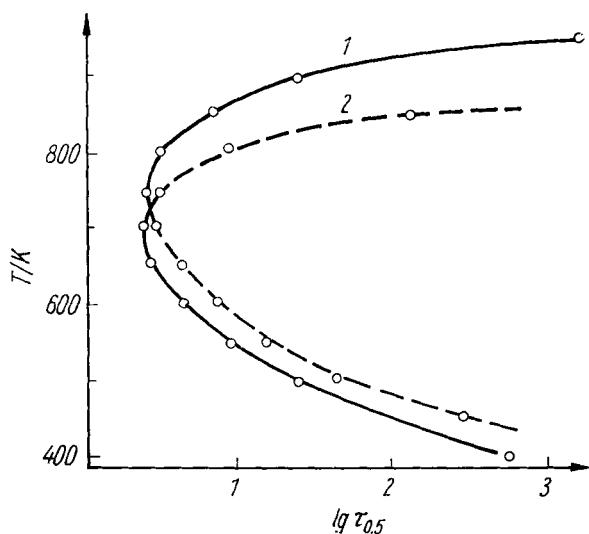
Fig. 7. Time logarithm for half-transformation of the phase 2 into stable modification 1 which
has no crystallographic correspondence with initial phase and into metastable phase a which
has such correspondence

correspondence of initial and appearing phases or base and appearing phases is in-
complete the process of their formation on the boundary with the surface may depend
on the degree of wetting of this boundary and on the change of surface energy. This
effect was considered by MIKHNEVICH; FLETCHER; HOBBS; FUKS; ZAREMBA et al. a.o.

If degree of dispersion of the base is high, its structure may vary from that of a base
of large crystallites (see SIROTA I). Hence the former may have crystallographic
similarity (size and orientational correspondence, crystallochemical affinity) with
the other, than the latter, metastable phase, stimulating its preferencial formation.

Substantial role may be played by nuclei having formed in canals, cavities, pores
(KAZACHKOVSKII 1948, SIROTA 1962, TURNBULL 1950). This nuclei may be of both
stable and metastable phase which depends on the structure and crystallochemical
peculiarities of the base.

XI. Influence of composition difference of inital and forming phases

As regards the mechanism and kinetics of new phase formation out of thermodynami-
cally supersaturated initial phase 2 a significant role is played by the probabilities of
concentration fluctuation in the initial phase caused by composition difference, and
by constituents of the work on formation of three- and two-dimensional nuclei
depending on elastic properties, difference of specific volumes, degree of ordering of
initial and appearing phases.

The influence of composition difference of initial and occuring phases may be
illustrated as follows. As may be seen from the state diagram (Fig. 8), from the so-
lution II of composition C_B of binary system A–B with decreasing temperature a stable
phase 1 may isolate (with composition AB), together with its metastable modifi-
cations $a, \ldots, a_n$ and metastable phase $A_3B_2(\eta)$. The results of computation of tem-
perature dependence of the work on formation of three- and two-dimensional nuclei
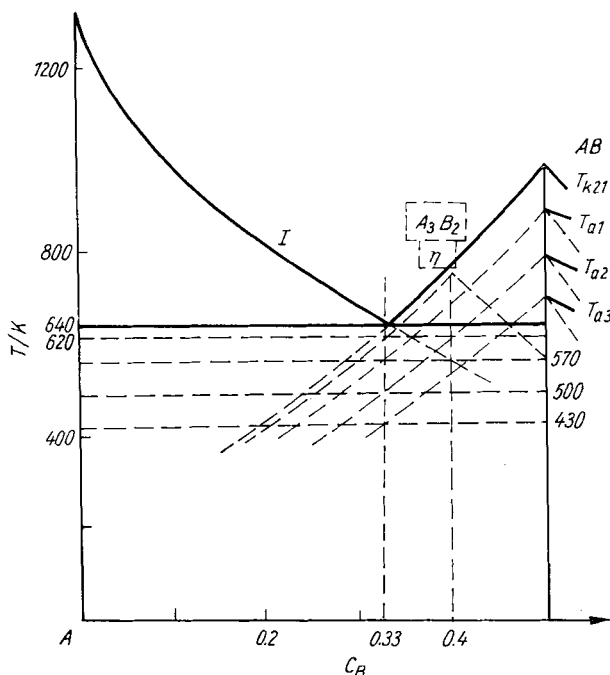
Fig. 8. State diagram: a stable compound AB (1) exists together with its metastable modifications a_1, a_2, a_3 and metastable compound A_3B_2 (η')

in the units of kT of all phases which can isolate from phase with $C_B = 0.33$, are shown in Figure 9. As may be seen from this figure the account of concentration fluctuation probability will result in the fact that excluding small supersaturations, when only stable phase forms, even in case of comparatively small or moderate supersaturation in the first instance metastable phase (η) is formed. The composition of the latter differs from that of initial phase less than from the composition of a stable phase AB. In case of large supersaturation, however, the least stable phase has the least total work on the nucleus formation; origination of this phase thus appears to be the most probable and transformation time involved is the shortest.

Computed curves A_3/kT, A_2/kT versus composition are shown in Figure 10 (concentration fluctuations are disregarded). The same curves with regard of concentration fluctuations, $A_3/kT + n_3B_3$, $A_2/kT + n_2B_2$ are shown in Figure 11. In Figure 12 there are presented half-transformation time logarithm curves for the transition of initial phase into stable and metastable phases computed for the state diagram of Figure 8.

Consideration of the role of concentration fluctuation probability, degree of undercooling and other kinetic factors permits us to ascertain why metastable state diagrams exist, e.g. Fe–Fe$_3$C (SIROTA) 1949; Fe–C (EPSTEIN; DARKEN, GURRY; ZHUKOV), Cd–Sb (SIROTA 1950a, b; MIROSHNICHENKO; PSARYOV).

Appearance of stresses E_g caused by elastic deformations arising from the volume change in the transformation process in this case of two- and multi-component systems may also significantly change the succession of formation of stable and metastable phases but mainly in the region of moderate supersaturation.
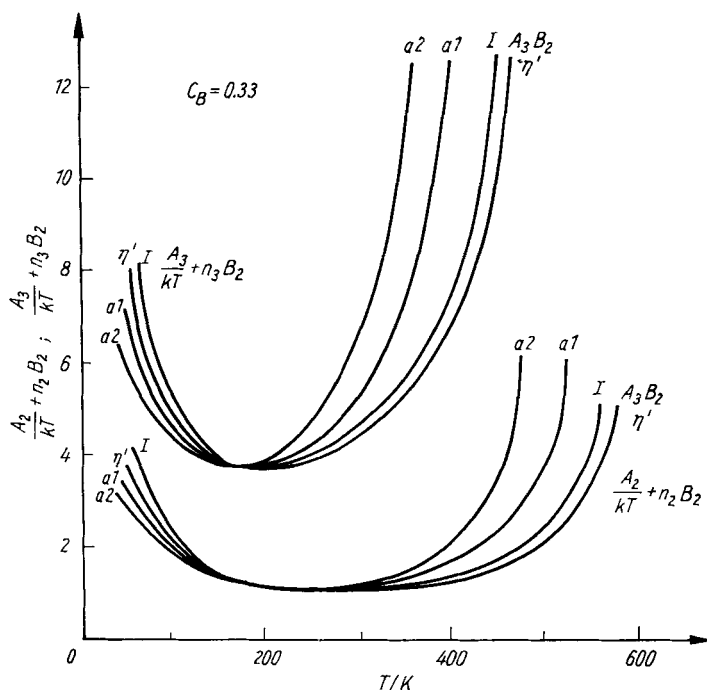
Fig. 9. Role of concentration fluctuation: temperature dependence of the work on formation of three-dimensional $\left(\dfrac{A_3}{kT} + n_3B_3\right)$ nuclei in the units of kT for stable modification 1 and metastable phases a_1, a_2, a_3 of compound AB, and metastable compound A_3B_2 (η') Initial phase 2 (Z) has a composition $C_{BZ} = 0.33$

XII. Role of multiplicity of active faces of the base and orienting influence of external fields

It should be noted that multiplicity factor and influence of magnetic electric, gravitational, and other external fields upon thermodynamic supersaturation and hence upon the transformation process play not the least role. Crystallochemical affinity of occurring phase with a base, inclusions, seeds or with initial phase is possible only parallel to certain planes and along certain directions. Thus the effect of this inclusions or seeds on the transformation process, stimulating predominant formation of a certain stable or metastable phase having the closest crystallochemical affinity for the bases will not only depend on the degree of supersaturation, but also on the factor of multiplicity of analogous active faces and directions, on the probability of their proper coincidence, characterized by the above mentioned factor $W_{2\eta}$, and also on the effective value of conjugated active surfaces.

The role of external magnetic and electric fields must also be taken into account since they exert influence upon the value of thermodynamical supersaturation and the probability of coincidence of interacting planes and proper directions in the crystalline bases, the forming nuclei and new-phase crystals. Preferential directions imposed by the fields may also orientate solitary atoms, molecules and especially clusters adjoining to the growing crystals of new phase.
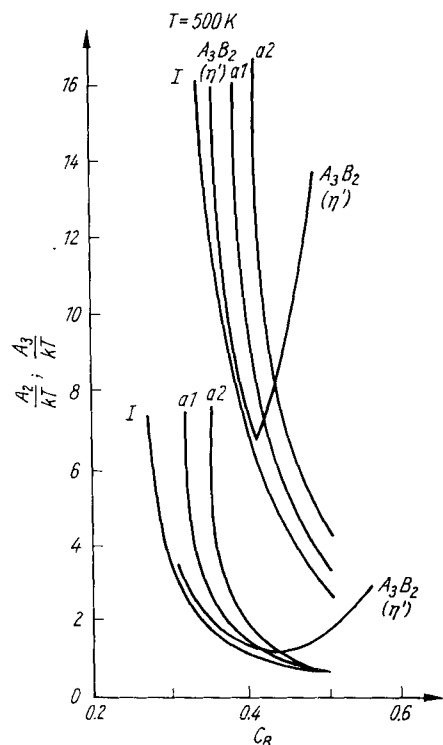
Fig. 10. Concentration dependence of the work on formation of three-dimensional (A_3/kT) and two-dimensional (A_4/kT) nuclei. (The phases are the same as in Figure 9) Concentration fluctuations are disregarded
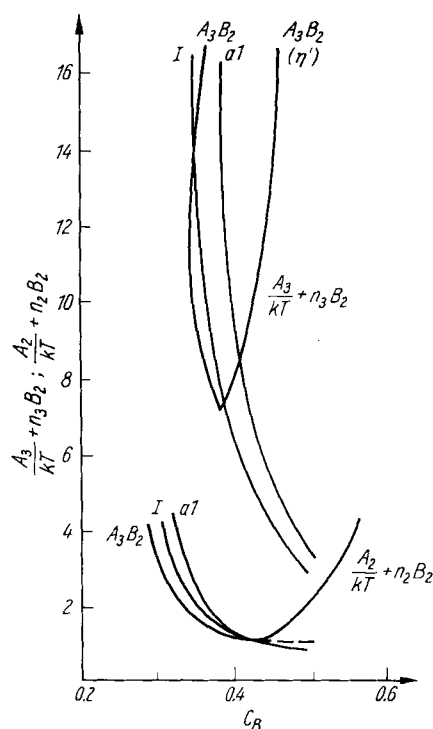
Fig. 11. The same as Figure 10, but concentration fluctuation are taken into account in the form $A_1/kT + n_3 B_3$, $A_2/kT + n_2 B_2$

A specific example may be considered when in presence of external electric and magnetic fields some or other stable or metastable phases predominantly form depending on the orientation of the fields with respect to bases. Probably this effect might be observed experimentally.[8])

XIII. Influence of thermodynamic supersaturation upon the formation of stable and metastable polymorphic modifications in chemical reactions, electrochemical processes and in process of film deposition

In chemical reactions, electrochemical processes, in case of condensation of vapour the value of thermodynamic supersaturation ΔZ may vary in wide range, and it is the value of ΔZ on which depends critical size of new-phase nuclei, work on their formation, rate of their formation and thus the rate of phase transition.

---

[8]) KAPITSA noted the role of orientating external fields on the example from archeology: determination of the position of pottery in furnaces according to its magnetization direction acquired in the Earth's magnetic field in the process of baking.

An example of similar influence is magnetization of marsh ores in the direction N–S in the process of their deposition in the terrestrial magnetic field.
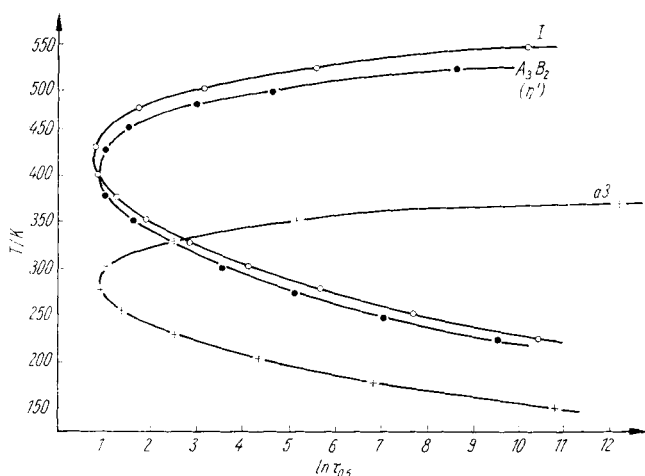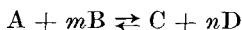
Fig. 12. Time logarithm of half-transformation of phase 2 (Z) of composition $C_{BZ} = 0.33$ into stable phase 1 and metastable modification a_3 and metastable compound A_3B_2 (η')

In chemical reactions which take place in liquids or in gaseous phase and in which solid phase C is formed,

$$A + mB \rightleftarrows C + nD$$

the degree of thermodynamic supersaturation depends on the deviation $K_2 - K_1$ of equilibrium constant of the reaction K_1 which is in case of solutions given by

$$K_1 = \frac{[A][B]^m}{[D]^n},$$

where [A], [B], [D] are concentrations of the components. In case of gaseous components the constant K_1 is given by

$$K_1 = \frac{p^A p_B^m}{p_D^n},$$

where p_A, p_B, p_D are vapour pressures. The supersaturation ΔZ is then

$$\Delta Z = RT \ln K_2/K_1.$$

In electrochemical processes the thermodynamic supersaturation ΔZ is determined by the deviation of potential difference between electrodes from its equilibrium value U_1:

$$\Delta Z = P(U_2 - U_1)$$

where F is Faraday constant.

The above consideration of the influence of thermodynamic supersaturation upon formation of stable and metastable phases and polymorphic modifications is valid in the case of chemical reactions, electrochemical processes, and also in the processes of crystal film deposition with the help of molecular beams (in the latter case $\Delta Z = RT \ln p_2/p_1$ where p_1 is equilibrium pressure of vapour of a given compound above the film, p_2 is the real pressure).

In the considered cases of chemical reactions and electrochemical processes formation of metastable phases in accordance with Ostwald's step rule will also take place when thermodynamic saturation is sufficiently high.

Important questions in electric crystallization had been studied by VOLMER (1922, 1934), GORBUNOVA (1935, 1957), GORBUNOVA and DANKOV (1949a, b), GORBUNOVA, IVANOVA and ZHUKOVA (1949), VAGRAMIAN (1950), KAISCHEW and BLIZNAKOV (1948), KAISCHEW, BUDEVSKII and MALINOVSKII (1955) and others.

An interesting question is the study of growth of electrolytic thin filaments. It was shown that the rate of their growth in isothermal conditions in a given electrolyte is determined mainly by potential difference and does not depend practically on the strength of current which influences only the thickness of the filament.

When thermodynamic supersaturation conditioned by concentration change of the components, their vapour pressure and temperature in chemical reactions, and also by the change of voltage in electrochemical processes, exceeds certain values, there appears possibility of formation and growth, in the first instance, of metastable polymorphic modifications, intermediate phases and states.

The dependence of work on formation of two- and three-dimensional nuclei on the degree of thermodynamic supersaturation, shown in Figure 6, is applicable in the cases considered above.

XIV. General regularities of the succession of formation of stable and metastable phases and limits of Ostwald's step rule validity

In all the cases considered a general regularity is preserved. If supersaturation or undercooling is small only stable phase is thermodynamically possible to form.

In a comparatively wide interval of intermediate values of thermodynamic supersaturation the transformation process and the type of the phase predominantly formed to a major extent is determined by supplementary kinetic factors: crystallographic correspondence of appearing and initial phase, presence of bases, having crystallochemical affinity with stable or some allowed metastable phase, concentration fluctuation probability, multiplicity factors of active faces of bases and forming phases, orientation by external fields, formation of nuclei in canals and pores of the base, etc.

In case of large values of thermodynamic supersaturation (e.g. undercooling), excluding may be the situations with great difference of specific volumes and/or composition of initial and appearing phases, in the first instant the farthest from equilibrium phases form. Among these metastable, non-equilibrium phases are those which can exist in equilibrium only under high pressure or in strong magnetic and electric fields.

Thus the famous Ostwald's step rule in the most general form holds only in case of sufficiently large thermodynamic supersaturations.

The above considerations allow with a sufficient certainty to reveal different physical factors causing the formation of metastable phases and to establish the conditions of Ostwald's step rule validity and failure.

XV. Several examples of formation of metastable polymorphics modifications and other phases in the process of crystallisation and phase transition

The ideas developed here are not only of physical interest but undoubtedly have a major practical significance. A considerable amount of available experimental

results proves the proposition presented in the article. Among them is, for example, deposition of thin films of cubic boron nitride and diamond in situation where graphitic modifications are thermodynamically stabler.

The formation of metastable phases results in complicated types of C-shaped curves of undercooled austenite in steels, supercooled solid ι olutions in alloy on the basis of titanium and zirconium, of dispersional solidification of aluminium alloys (reference book by NOVIKOV; FRIDLANDER et al.).

Stability of undercooled austenite of the majority of complexly alloyed steels containing carbide-forming elements (in contrast to carbon steel) is as a rule described by complicated C-shape curves (DAVENPORT, BAIN).
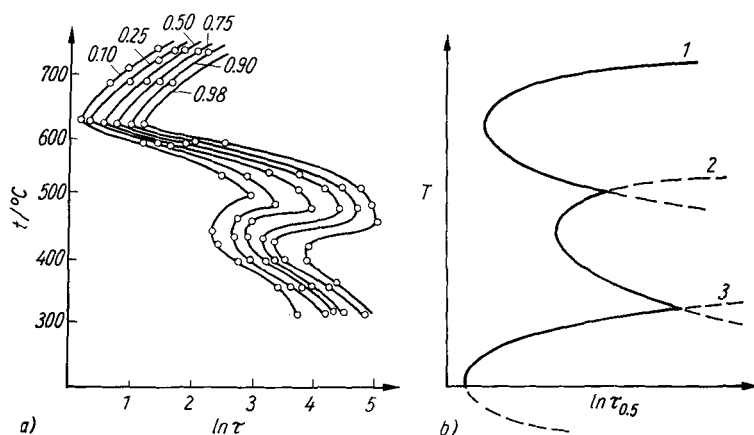

Fig. 13. a) Transformation of undercooled austenite of steel (1 % C, 1.5 % Cr): time logarithm for transformation of 10, 25, 50, 75, 90, and 98 % of mass; b) Schematic curves of time logarithm for half-transformation of austenite of chromium high frost-resistent steel. 1 — isolation of carbide $(Fe_2Cr)_7C_3$; 2 — isolation of carbide $(FeCr)_3C$; 3 — formation of trostomartensite

The term "complicated type" of C-curves of stability has been introduced by SADOVSKII and was primarily applied to steels; now its meaning has widened. An example of complicated-type C-curve of stability of initial undercooled phase is that of undercooled austenite of high-carbon chromium bearing steel (1.5% Cr, 1% C), as shown in Figure 13a (SIROTA, 1962). Also shown schematically (Fig. 13b) are simple stability curves of undercooled austenite with respect to the isolation of stable and metastable phases (modifications) of appearing carbides. This figure explains, how complicated C-curve forms, being the result of simple C-curves for various modifications. Comparison of the experimental complicated C-curve with computed ones allows one to clear up reasons and underline factors conditioning the complication of C-curves.

Let's remark that isolation of free carbon out of undercooled austenite as well as in the case of cementite graphitization for sufficiently large supersaturaticns, is possible in the form of its metastable polymorphic modifications, including diamond-like.

Similar conditions determine possibility of formation of metastable phases in case of thin film evaporation upon sufficiently undercooled bases (e.g. during deposition of carbon, boron nitride and compounds $A^{III}B^V$ there may form, respectively, diamond, cubic boron nitride and metallic films.

Successive isolation of stable and metastable phases — Guinier-Preston's zones — is realized in the ageing of duralumin (see e.g. review by BUJNOV and ZAKHAROVA, KOMAR, BUJNOV, monograph by ZAKHAROVA).

In case of relatively small undercooling stable Θ phase is isolated ($CuAl_2$). At greater undercooling metastable Θ' phase forms, and at still lower temperature Θ'' phase forms. When ageing is completed (i.e. metastable phase has been isothermally isolated), subsequent heating to the temperature lower than equilibrium miscibility level but higher than that for metastable phase leads to dissolution of metastable phase. Thus may be explained the recovery phenomenon — GAILER's effect (GAILER; SIROTA 1945 a). Further soaking at the pointed higher temperature leads to isolation of stable Θ phase.

The example of complicated-type C-shaped curves for light aluminium alloys, etc. may be found in reference book by NOVIKOV.

The above consideration explains the peculiarities of composition change of carbides during tempering of hardened, e.g. chromium steels, and in the isothermal transformation of undercooled austenite of these steels. At low temperatures (i.e. great thermodynamic supersaturations) predominantly metastable carbide phase is formed.
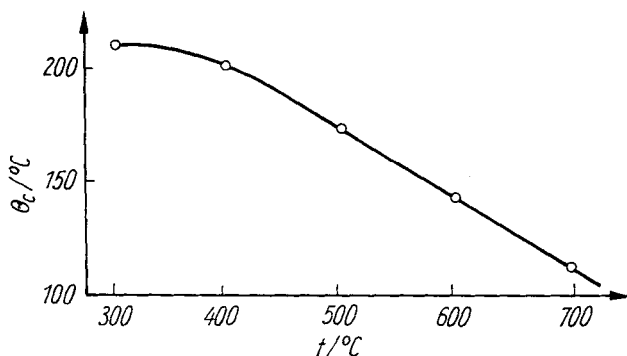

Fig. 14. Change of Curie point θ of the isolating carbides as a function of transformation temperature t (°C) (tempering of hardened steel 1 % Cr; 1 % C)
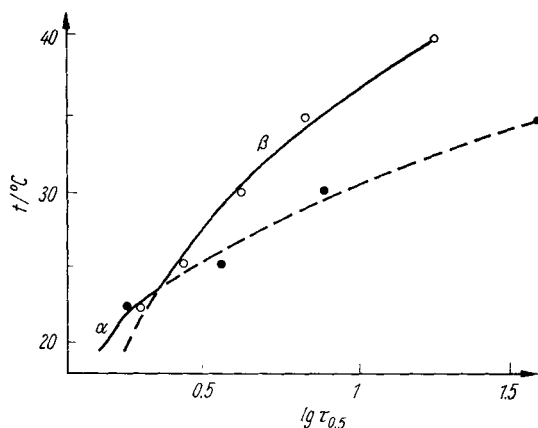

Fig. 15. Time logarithm of half-transformation of amorphous trilaurine into stable β and metastable α phases as a function of temperature (computed with the data of RAVITCH et al.)

In a number of our works the composition of carbides, isolating in isothermal transformation of austenite and during tempering of hardened steels had been controlled by the change of Curie point (magnetic transition temperature) (SIROTA 1939, 1948) (Fig. 14). The observed regularities of carbide composition and structure change had been explained on the basis of similar ideas.

Persuasive example proving the views presented above is the formation of stable modification at relatively small undercooling and metastable α-modification at large undercooling in the process of isothermal crystallization of trilaurine, investigated by RAVICH et al. (Fig. 15).

Study of crystallization of thin amorphous films of stibium (SHALNIKOV), germanium (SIROTA, DENIS), aluminium oxide (SIROTA, SHOKHINA) proves that at sufficiently low temperatures metastable phases or metastable polymorphic modifications crystallize and, conversely, at higher temperatures, stable modifications of redundant phase form in the first instance.

Investigation of crystallization of thin $A^{III}B^{V}$-compound films shows that in case of great undercoolings metastable phases form including metallic superconductive phases (see collected articles edited by ALEKSANDROV and PETROSIAN; PALATNIK et al.; PALATNIK).

An interesting example of metastable phase formation was given by R. W. NERZ.

Formulation by Ostwald of his step rule has become an important stimulus in the study of formation of metastable phases and different metastable polymorphic modifications. Investigations presented above allowed to establish the limits of Ostwald's step rule validity, to find new regularities, to determine the conditions and succession of formation of stable and metastable phases. All these opens wide prospects of practical application of the established regularities.

The purpose of the present work has been further development of this important problem — experimental and theoretical analysis of the conditions leading to formation of metastable polymorphic modifications, phases and states.

References

ALEKSANDROV, A. P.: Nauka strane, Moscow 1983
ALEKSANDROV, L. N.: Kinetika obrasovanija i struktury tverdykh sloyov, Novosibirsk 1972
ALEKSANDROV, L. N., PETROSIAN, V. I.: Plenki dla mikroelektroniki, Novosibirsk 1977
ANOSOV, W. Ja.: Izv. sekt. Fiz-chim. analiza 22, 67, 1953
ANOSOV, W. Ja., POGODIN, S. A.: Osnovnyye nachala fiziko-khimicheskogo analiza, Moscow 1947
ANOSOV, V. Ja., OZEROVA, M. U., FIALKOV, Yu. A.: Osnovy fiziko-khimicheskogo analiza, Moscow 1973
ARKHAROV, V. I.: Okisleniye metallov pri vysokikh temperaturakh, Sverdlovsk-Moscow 1945
ARKHAROV, V. I.: Fiz. Met. i Metalloved 12, No 6 (1961)
ARTEMJEV, V. N.: Metod kristallizatii Sharov. Tr. Petr. Obchestva Estestvoispitatelei 37, 59 (1914)
AVRAANI, J.: J. Chem. Phys. 7, 103 (1939); 8, 212 (1940)
BAJKOV, A. A.: Sobraniye trudov 1—5, Moscow-Leningrad 1948—1952
BALARIN, M., SCHENK, M.: phys. stat. sol. 17, 91 (1966)
BARABOSKHIN, A. N., KOSIKHIN, L. T.: Kristallizatsiya i fazovyye prevrascheniya, Minsk 1971, pp. 118—125

BARTENEV, G. M.: Zh. Fiz. Chim. **34**, 3 (1960)

BAZAROV, J. P.: Termodinamika, Moscow 1976

BECKER, R.: Z. Metallkde. **29**, 245 (1937); **32**, 128 (1938)

BECKER, R., DÖRING, W.: Ann. Phys. **24**, 719 (1935)

BELENKII, V. Z.: Geometriko-veroyatnostnyye modeli kristallizatsii, Moscow 1980

BELOV, A. F., GLAZOV, V. H., POTEMKIN, A. Ya., AKOPIAN, R. A.: Doklady AN SSSR **259**, 135 (1981)

BELOV, K. P.: Magnitnyie Prevrashcheniya, Moscow 1959

BELOV, B. V.: Struktura ionnykh kristallov metallicheskikh faz, Moscow 1947

BERTAUT, F. J.: Phys. Rad. **12**, 252 (1951)

BLANTER, M. Ye.: Zh. Tekhn. Fiz. **17**, 1731 (1947)

BLIZNAKOV, G. M.: Bulg. AN, ser. fiz. **6**, 301 (1951)

BLIZNAKOV, G. M.: Kristallografiya 4, No 2 (1959)

BLIZNAKOV, G. M.: Godishnik na Sof. Univ. Phys.-Mat. **2**, 69 (1956)

BOCHVAR, A. A.: Issledovaniye mekhanizma i kinetiki kristallizatsii splavov elektricheskogo tipa, Moscow 1935

BOCHVAR, A. A., GOREV, K. V.: Izv. sekt. fiz.-khim. analiza, 8, 283 (1936)

BOCHVAR, A. A., TAMMAN, G. A.: Vestnik Metallopromyshlennosti N 5 — 6 (1927)

BOKII, G. B.: Vvedeniye v kristallokhimiyu, Moscow 1960

BORELIUS, G.: Ann. Phys. **33**, 517 (1938)

BORELIUS, G.: Ann. Phys. **28**, 507 (1937)

BORISOV, V. T., DUKHIN, A. I.: in: Mekhanism i kinetika kristallizatsii Minsk 1969, pp. 169 — 181

BROWN, P. J., FORSYTH, J. B.: The crystal structure of solids, London 1973

BROWN, P. J.: Acta Cryst. **10**, 133 (1967)

BUGAKOV, V. Z.: Diffusiya v metallakh i splavakh, Moscow-Leningrad 1949

BURTON, W. K., CABRERA, N., FRANK, F. C.: Phys. Trans. **243**, 299 (1951)

BUYNOV, N. N., ZHURAVLEV, M., KOMAR, A. P., CHUFAROV, G. I.: Doklady AN SSSR **22**, 27 (1939)

BUYNOV, N. N., ZAKHAROVA, R. R.: Raspad metallicheskikh tverdykh rastvorov, Moscow 1964

BYKHOVSKII, A. I., LARIKOV, L. N., OVSIYENKO, D. E.: Kristallografiya 6, 284 (1961)

CAHN, J. N.: Acta Metallurg. **9**, 795 (1961); **10**, 179 (1962)

CHATELIER, H., le: Compt. Rend. **9**, 118, 698 (1894)

CHERNOV, A. A.: Uspekhi Fiz. Nauk **73**, No 2 (1961)

CHERNOV, D. K.: Zapiski rus. tehn. obshchestva No 7, 339 (1868)

CHERNOV, D. K.: Staleliteinoye delo, St.Petersburg 1898

CHERNOV, D. K.: Izbrannye trudy, ed. by V. D. SADOVSKII, compiled by A. S. FEDOROV, Moscow 1983

CHRISTIAN, J. W.: Transformations in metals and alloys, second ed., pt. I, Oxford 1975

DANILOV, V. I.: Stroyeniey i kristallozatsiya zhidkosti, Kiev 1956

DANILOV, V. I., KAMENETSKAYA, D. S.: Zh. Fiz. Khim. **XXII**, 69, (1948)

DANILOV, V. I., KAZACHKOVSKII, O. D., LAPKOVSKII, I. M.: Zh. Eksp. Teor. Fiz. 18, No 10, 886 (1948)

DANILOV, V. I., RADCHENKO, I. V.: Zh. Eksp. Teor. Fiz. 7, 1153 (1937)

DANKOV, P. D.: Doklady AN SSSR 23, 548 (1938)

DADKOV, P. D.: Izv. Sekt. Fiz. Khim. analiza 16, 82 (1941)

DARKEN, L. S., GURRY, R. W.: Physical Chemistry of Metals, New York 1953

DAVENPORT, E. S., BAIN, E. C.: Trans. AIME **90**, 117 (1930)

DEHLINGER, U.: Chemische Physik der Metalle u. Legierungen, Leipzig 1939

DEHLINGER, U., BORELIUS, G.: Handbuch der Metallphysik, Bd. I. Leipzig 1939

DUNNING, W. J.: in: Chemistry of the solid state, ed. W. E. GARNER, London 1955

EHRENFEST, P.: Communication Leiden, Suppl. 756, 1933

EPSTEIN, P.: The Alloys of Iron and Carbon, New York, 1936

FARKASH, L.: Z. Phys. Chem. **125**, 236 (1927)

FEDOROV, A. S.: Tvortsy nauki o metalle, Moscow 1980

FINK, W., SMITH, D.: Met. Techn. No 3, 95 (1939)

FLETCHER, N. H.: J. Chem. Phys. **31**, 1136 (1959)

FRANK, F. C., VAN DER MERVE, J. H.: Proc. Roy. Soc. **198**, 216 (1949)

FRANK, F. C.: Acta Metallurg. **1**, 15 (1953)

FRANK, F. C., READ, W. T.: Phys. Rev. **79**, 722 (1950)

FRENKEL', Ya. I.: Izv. Sect. Fiz.-Khim. Analiza **16**, 50 (1941)

FRENKEL', Ya. I.: J. Chem. Phys. **1**, 200, 538 (1939)

FRENKEL', Ya. I.: Zh. Ekop. Teor. Fiz. **16**, 1 (1948)

FRENKEL', Ya. I.: Kineticheskaya teoriya zhidkosti, Leningrad 1945

FRIDLANDER, I. N., STEPANOVA, M. G., SEFUKOV, O. A., BRUKHOVETZ, A. A.: Aluminiyevye splavy, Moscow 1968, pp. 226 – 230

FRIDLANDER, I. N.: Issledovaniye form rosta kristallov v zavisimosti ot skorotsti okhlazhdeniya, Moscow 1948

FRIDLANDER, I. N.: Aluminievye deformiruemye konstruktsionnye splavy, Moscow 1979

FUKS, N. A.: Uspekhi Fiz. Nauk **15**, 496 (1935)

GAYLER, M. L. V.: J. Inst. Metals **29**, 212 (1922)

GIBBS, J. W.: Thermodynamische Studien, aus dem Englischen übersetzt von W. OSTWALD, Leipzig 1882

GIBBS, J. W.: Termodinamicheskiye raboty, V. K. SEMENCHENKO, ed. Moscow 1950

GINZBURG, V. L.: Zh. Eksp. Teor. Fiz. **17**, 838 (1947)

GLIVENKO, V. I.: Kurs teorii veroyatnostey, 1939

GNEDENKO, B. V.: Kurs teorii veroyatnostey, Moscow 1961

GÖLLER, F., SACHS, G.: Z. Physik **77**, 281 (1932)

GORBUNOVA, K. M.: Izv. AN SSSR No 5 – 6, 1175 (1935)

GORBUNOVA, K. M.: Sbornik Rost Kristallov **1**, 1957

GORBUNOVA, K. M., DANKOV, P. D.: Uspekhi Kkumiu **17**, 710 (1948)

GORBUNOVA, K. M., DANKOV, P. D.: Zh. Fiz. Khim. **23**, 616 (1949)

GORBUNOVA, K. M., ZHUKOVA, A. I.: Zh. Fiz. Khim. **23**, 605 (1949)

GORSKII, F. K.: Zh. Eksp. Teor. Fiz. **6**, 278 (1936)

GUGGENHEIM, E. A.: Mixtures, Oxford 1952

GUNIER, A.: Compt. Rend. **206**, 1641 (1938)

HARDY, H. K., HEAL, T. Y.: The Mechanism of Phase Transformation in Metals, London 1956

HARDY, H.: J. Inst. of Metals **77**, 5 (1950)

HOBBS, P. V.: Ice Physics, Oxford 1974

HOLLOMAN, Y. H., TURNBULL, D.: Progress in Metal Physics **4**, 333 (1953)

HUME-ROTHERY, W., REYNOR, G. V.: The Structure of Metals and Alloys, London 1962

IVANOV, O. S.: Izv. AN SSSR OKhN. No 4, 192 (1944)

IVANTSOV, G. P.: DAN SSSR **58**, 567 (1947)

JACOBS, P., TOMPKINS, F.: Chemistry of the Solid State, London 1955

JOHANSON, W. A., MEHL, R. F.: Tr. AIME **135**, 416 (1939)

KAISIHEW, R., BLIZNAKOV, G.: Compt. Rend. Acad. Bulg. **1**, No 2 – 3, 23 (1948)

KAISCHEW, R., BUDEVSKI, E., MALINOVSKI, J.: Z. Phys. Chem. **204**, 348 (1955)

KAISCHEW, R. A., STRANSKI, I. N.: Z. Phys. Chem. **170**, 295 (1934)

KAPITSA, P. L.: Private communication

KAZACHKOVSKII, O. D.: Sbornik nauchnykh rabot laborat. metallofiziki, Kiev 1948, p. 76

KAUFMAN, L., BERNSTEIN, H.: Computer calculation of phase diagrams, New York 1970

KAZEEV, S. A.: Metallurg. **6**, 43 (1936)

KAZEEV, S. A.: Kinetika v prilozheniyakh k metallovedeniyu, Moscow 1956

KHACHATURIAN, A. G.: Teoriya Fazovykh prevraschenii i Struktura tverdykh rastvorov, Moscow 1974

KHAMSKII, E. V.: Kristallizatsiya iz rastvorov, Leningrad 1967

KIRKWOOD, J. G., BUFF, J.: J. Chem. Phys. **17**, 338 (1949)

KLEBER, W.: Einführung in die Kristallographie, Berlin 1965

KOLMOGOROV, A. N.: Izv. AN SSSR, Mat. No 3, 365 (1937)

KOMAR, A. P.: Izv. AN SSSR Fiz. **11**, 497 (1947)

KREBS, H.: Grundzüge der anorganischen Kristallchemie, Stuttgart 1968

KUBASCHEWSKI, O.: Phase Stability in Metals and Alloys, New York etc. 1967.
KURDYUMOV, G. V.: Rentgenografiya i primenenie rentgenovskikh luchey, Moscow 1936
KURDYUMOV, G. V.: Zh. Tekhn. Fiz. **18**, 999 (1949)
KURDYUMOV, G. V., SACHS, G.: Vestnik metallo-promyshlennosti No 9−10, 165 (1930)
KURDYUMOV, G. V., SACHS, G.: Z. Physik **64**, 325 (1930)
KURDYUMOV, G. V.: K teorii martensitnogo prevrashcheniya Problemy metallovedeniya
    i faz metallov, No 3, Moscow 1952
KURNAKOV, N. S.: Vvedeniye v Fit. Khim. analiz, Moscow 1941
KUZNETSOV, V. D.: Fizika tverdogo tela **1**, Tomsk 1937
LAAR, L. J. VAN: Die Thermodynamik einheitlicher Stoffe und binärer Gemische, Gröningen
    1936
LANDAU, L. D.: Zh. Eksp. Teor. Fit. **19**, 137, 627 (1937)
LANDAU, L. D., LIFSHITS, E. M.: Statisticheskaya Fizika, pt 1, Moscow 1976
LERINMAN, R. M., BUINOF, N. N.: FMM **10**, 374 (1960)
LEMLEIN, G. G., DUKOVA, E. D.: DAN SSSR **102**, 77 (1955)
LEMLEIN, G. G.: Vestnik AN SSSR, **4**, 119 (1945)
LEONTOVICH, M. A.: Vvedeniye v termodinamiku, Moscow 1951
LIPILIN, I. P.: Kachestvennaya Stal., No 9, 1935
LUMSDEN, J.: Thermodynamics of Alloys, London 1952
MAKAROV, E. S.: Stroyeniye tverdykh faz s peremennym chislom atomov v elementarnoy
    yacheike, Moscow 1947
MAKSIMOVA, O. P.: Problemy metallovedeniya i fizika metallov, Moscow 1952
MEHL, R. F., SMITH, D.: Metals Technology, No 521 (1934)
MEZHIDOV, V. I., GUROV, A. I., KRASNOBRIZHEV, V. G.: Zh. Fiz. Khim **52**, 52, 1965 (1978)
MIKHNEVICH, G. L.: Zh. Eksp. Teor. Fiz. **9**, 215 (1939)
MIKHNEVICH, G. L.: Kolloidny Zhurn. **21**, No 1, No 3, No 4 (1959)
MIROSHNICHENKO, I. S.: Zakalka iz zhidkogo sostoyaniya, Moscow 1982
MLODZEYEVSKII, A. B.: Termodinamika i teoriya faz Moscow-Leningrad 1922
MLODZEYEVSKII, A. B.: Geometricheskaya termodinamika, Moscow 1956
MLODZEYEVSKII, A. B.: Teoriya faz, Moscow 1937
MOTT, N. F., NABARRO, F. R. N.: Proc. Roy. Soc. **52**, 86 (1940)
MÝL, I.: in: Rost Kristallov **5**, 246 (1965)
NABARRO, F. R. N.: Proc. Phys. Soc. **52**, 90 (1940); Proc. Roy. Soc. A. **175**, 519 (1940)
NERZ, R. W.: Tr. Farad. Soc **5** (1949)
NIKITINA, G. V., ROMANENKO, V. N.: Izv. AN SSSR, No 6,156 (1964)
NOVIKOV, I. I., ed.: Diagrammy isotermicheskogo raspada rastvora v aluminiyevych
    splavakh, Moscow 1973
NÝVLT, T.: Collect. Czech. Chem. Comm. No 28, 2269−2279 (1963)
ORIANI, R. A.: J. Chem. Phys. **18**, 575 (1950)
OSTWALD, W.: Grundriß der Allgemeinen Chemie, Leipzig 1899
OVSIYENKO, D. YE.: Problemy sovremennoy kristallografii, Kiev 1975, pp. 127−149
PALATNIK, L. S.: Doklady AN SSSR, **82**, No 6 (1952)
PALATNIK, L. S., FUKS, M. I., KOSEVICH, V. M.: Mekhanizm obrazovaniya i substruktura
    kondensirovannykh plenok, Moscow 1972
PAUFLER, P.: Phasendiagramme, Berlin 1981
PAUFLER, O., LENCHNER, D.: Kristallografische Grundbegriffe der Festkörperphysik,
    Berlin 1975
PINÉS, B. Ya.: Izv. sect. fiz.-khim. analiza, **16**, 66 (1941)
PINÉS, B. Ya.: Ocherki po metallofizike, Kharkov 1961
POUND, G. M.: Ind. and Eng. Chem. **44**, 1278
PRESTON, G. D.: Phil. Mag. **26**, 856 (1938)
PSARYEV, V. I.: Dokt. dissertatsiya, Dnepropetrovsk 1956
PSARYEV, V. I., DOBRIDENI, K. A.: Fiz. Met. **18**, No 1, 47 (1964)
RAVICH, G. B., TSURINOV, G. G., VOLNOVA, V. A.: Izv. AN SSSR, No 6, 581 (1945)
REISS, H.: J. Chem. Phys. **20**, 1216 (1952)
RODIGIN, V. N.: Zh. Techn. Fiz. **22**, 8 (1952)

Rozeboom, B.: Die Heterogenen Gleichgewichte vom Standpunkt der Phasenlehre, Braunschweig 1901

Rudman, P. S., Stringer, J., Jaffe, R. J.: in: Phase Stability of Metals and Alloys, New York etc. 1967

Sadovskii, V. D.: Izv. AN SSSR, No 3, 219 (1945)

Semenchenko, V. K., Pokrovskii, N. L.: Uspekhi khimii 6, 945 (1937)

Semenchenko, V. K.: Zh. Fiz. Khim. 19, 9 (1945)

Semenchenko, V. K., a: Poverkhnostnyye yavleniya v metallakh i splavakh, Moscow 1957

Semenchenko, V. K., b: in: Fizika i Fiziko-Khimicheskii analiz, Moscow 1957

Semenchenko, V. K.: Izbrannyye glavy teoreticheskoy fiziki, Moscow 1966

Semenchenko, V. K.: Izbrannyye glavy teoreticheskoy fiziki, Moscow 1968

Semenchenko, V. K., Petrovskii, V. A.: in: Kristallozatsiya i fazavyye prevrashcheniya, Minsk 1971

Shalnikov, A. I.: Private communication

Shreder, I. F.: Gorny Zhurnal 11, 272 (1890), 11, 449 (1893)

Shterenberg, A. A.: in: Rost Kristallov 5, Moscow 1965

Silcock, J. M., Davis, M. H., Hardy, H. K.: The Mechanism of the Phase Transitions in Metals, London 1955

Silcork, J. M., Heal, T. Y., Hardy, H. K.: J. Inst. Met. 82, 239 (1954)

Sirota, N. N.: Thesis, MIS 1939; Trudy MIS No 24, 161 (1939), No 13, 287 (1939)

Sirota, N. N.: Doklady AN SSSR 36, No 6, 192 (1942)

Sirota, N. N.: Doklady AN SSSR 39, No 3, 111; No 8, 322, 355; 40, No 6, 265 (1943)

Sirota, N. N.: Doklady AN SSSR 44, No 8, 359 (1944)

Sirota, N. N.: Doklady AN SSSR 52, No 5, 337; 343 (1945)

Sirota, N. N.: Doklady AN SSSR 51, No 4, 295, 52, No 2, 152 (1946)

Sirota, N. N., a: K termodinamike tverdykh rastvorov. I. Soveshchaniye po kristallokhimii Moscow (1948), p. 106

Sirota, N. N., b: Doklady AN SSSR 59, No 3, 519; No. 7, 1309 (1948)

Sirota, N. N., c: Trudy MIS No 26, Moscow 1948, p. 111

Sirota, N. N., d: Zh. Tekhn. Fiz. 18, No 9, 1136 (1948)

Sirota, N. N.: Doklady AN SSSR 64, No 5, 697 (1949)

Sirota, N. N., a: Doklady AN SSSR 74, No 5, 971; No 6, 1105 (1950)

Sirota, N. N., b: Izv. Sekt. Fiz. Khim. Analiza, 20, 326 (1950)

Sirota, N. N.: Trudy NTO, Ch. M. 6, 152 (1955)

Sirota, N. N.: in: Fizika i Fiziko-Khim. analiz, No 1, Moscow 1957, p. 299

Sirota, N. N.: Trudy NTO, Ch. M. 13, 108 (1958)

Sirota, N. N., 8: in: Rost Kristallov 3, Moscow 1961

Sirota, N. N., b: Teoriya Rosta Kristallov, Thesis, Minsk 1961

Sirota, N. N.: Kristallizatsiya i Fazovyye perekhody, Minsk (1962), pp. 82, 402

Sirota, N. N., a: Mekhanizm i kinetika kristallizatsii, Minsk 1969

Sirota, N. N., b: Termodinamika i statisticheskaya Fizika, Minsk 1969

Sirota, N. N.: Fiziko-Khimicheskaya priroda faz peremennogo sostava, Minsk, 1970

Sirota, N. N.: Trudy I Japan Soviet symposium on physical Chemistry of Metallurgic processes, 1967, Moscow 1969

Sirota, N. N.: in Kristallizatsiya i Fazovyye prevrashcheniya, Minsk 1971, p. 333

Sirota, N. N.: in: Kinetika i mekhanizmy kristallizatsii, Minsk 1973, p. 188

Sirota, N. N.: in: Magnitnyye plenki, Minsk 1974, p. 7

Sirota, N. N., Denis, V. A.: Kristall u. Technik 6, No 3, 381 (1971)

Sirota, N. N., Stokhina, G. N.: Kristall u. Technik 9, No 8, 913 (1974)

Skapski, A. G.: Acta Metallurg. 4, 576 (1956)

Skripov, N. N.: Nestabil'naya zhidkost, Moscow 1972

Smolenskii, G. A., Pasynkov, R. Ye.: Doklady AN SSSR 79, 431 (1951)

Smoluchowski, M.: Sitz. Ber. A. d. W. Wien, IIa 124, 339 (1915)

Smoluchowski, M.: Phys. Z. 17, 557, 585 (1916)

Soloyvov, Yu. I.: Ocherki istorii Fiziko-Khimicheskogo analiza, Moscow 1955

Stanley, H. E.: Introduction to phase transitions and critical phenomena, Oxford 1971

STARK, B. V., MARKIN, I. L., ROMANSKII, A. V.: Trudy MIS **7**, 5 (1935)
STEPANOV, N. I., KORNILOV, I. I.: Izv. Sect. Fiz. Khim. Analiza **10**, 79, 97 (1937)
STRANSKI, I. N.: Z. Phys. Chem. **136**, 259 (1920)
STRANSKI, I. N., KAISCHEW, R. A.: Z. Phys. Chem. **26**, 107 (1934)
STRANSKI, I. N., KAISCHEW, R. A.: Uspekhi Fiz. Nauk **21**, 408 (1939)
TAMMANN, G.: Kristallisierung und Schmelzung, Leipzig 1902
TAMMANN, G.: Lehrbuch der heterogenen Gleichgewichte, Braunschweig 1924
TAMMANN, G.: Aggregatzustände, Leipzig 1931
TAMMANN, G.: Z. Allg. Anorg. Chem. **214**, 407 (1933)
TANANAYEV, I. V.: IX Kurnakovskoe Chtenie, Moscow 1957
TERLETSKII, Ya. P.: Statisticheskaya Fizika, Moscow 1973
TODES, O. M.: Zh. fiz. khim. **14**, 1224 (1940)
TOLMAN, R. C. J.: J. Chem. Phys. **17**, 333 (1949)
TSEDRIK, M. S.: in: Kristallizatsiya i Fazovyye perekhody, Minsk 1962
TURNBULL, D.: J. Chem. Phys. **18**, 198 (1950)
TURNBULL, D.: J. Appl. Physics **21**, 1022 (1950)
TURNBULL, D., FISCHER, Y. C.: J. Chem. Phys. **17**, 71 (1949)
TURNBULL, D., VONNEGUT, B.: Ind. Eng. Chem. **44**, 1292 (1952)
URAZOV, G. G.: Izv. IFKh **2**, 97 (1922)
VAGRANYAN, A. T.: Electroosazhdeniye metallov, Moscow 1950
VATOLIN, N. A., VESELOVA, S. I.: F.M.M. **37**, 181 (1974)
VITTORF, N. M.: Teoriya Splavov, St. Petersburg 1909
VOGEL, R.: Die heterogenen Gleichgewichte, Leipzig 1959
VOLMER, M.: Z. Electrochem. **35**, 555 (1929)
VOLMER, M.: Kinetik der Phasenbildung, Leipzig 1939
VOLMER, M., FLOOD, H.: Z. Phys. Chem. A. **170**, 273 (1934)
VOLMER, M., WEBER, A.: Z. Phys. Chem. **119**, 277 (1925)
VONSOVSKII, S. V.: Doklady AN SSSR **27**, 550 (1940)
VONSOVSKII, S. V.: Izv. AN SSSR, Fiz. **11**, 485 (1947)
WASSERMANN, G.: Arch. Eisenhüttenwes. **11**, 89 (1937)
ZAKHAROVA, M. I.: Atomno-kristallicheskaya struktura i svoystva metallov i splavov,
      Moscow 1972
ZAREMBA, V. G., VASILKOVSKAYA, N. V., EFIMOVA, V. P.: in: Mekhanism i kinetika
      kristallizatsii, Minsk 1969
ZELDOVICH, Ya. B.: Zh. Eksp. Teor. Fiz. **12**, 525 (1942)
ZHDANOV, G. S.: Fizika Tverdogo Tela, Moscow 1961
ZHUKOV, A. A.: Geometricheskaya Thermodinamika Splavov Zheleza, Moscow 1979

Author's address:

Professor N. N. SIROTA
Member of the BSSR Academy of Sciences, MGMT, Department of Physics
ul. Pryanishnikowa, 19
125 008 Moscow A 8, USSR