ELSEVIER

Thermochimica Acta 254 (1995) 1–10

thermochimica
acta

Localization phenomena in heterogeneous chemical kinetics with respect to a geometric–probabilistic description

A. Korobov

Kharkov University, P.O. Box 10313, Kharkov 310023, Ukraine

Received 27 May 1994; accepted 31 August 1994

Abstract

In discussing the interconnection between the preferred local occurrence of a solid-phase chemical reaction and the geometric–probabilistic description of reaction kinetics, it is shown that the original solid reagent must be represented in this description in the proper manner. A way of doing this for an original single crystal is suggested, through subsequently separating the negative crystal growth and the two-dimensional advance of the front along the surface with the account of its translational symmetry in terms of Wigner–Seitz cells. Symmetry considerations in favor of the proposed essentially two-dimensional approach are discussed.

Keywords: Geometric–probabilistic description; Planigon; Reaction front advance; Symmetry; Wigner–Seitz cell

1. Introduction

The use of the geometric–probabilistic formalism [1–5] originally developed for phase transitions in describing solid-phase reaction kinetics is justified because a solid-phase chemical reaction is localized, this fact being represented in terms of the formation and growth of nuclei. The chemical essence of this preferred situation was clearly interpreted by Langmuir [6]: the very first reaction event promotes substantially the entry of neighboring atoms into a reaction. Otherwise, a reaction may not proceed, or may proceed in a non-localized manner, i.e. with the formation of a solid solution rather than individual phases. However, in discussing the causes

SSDI 0040-6031(94)02110-4

and effects, the energetic inhomogeneity of an original solid reagent is emphasized not infrequently as the main factor determining the local promotion of reactivity.

In a formal respect, this shift of emphasis manifests itself in that the nucleus is associated simply with some energetic inhomogeneity (whereas according to Langmuir it may well appear on the originally homogeneous surface) and the growth of nuclei is considered with respect to formation of the new phase alone, the original solid phase not being represented in corresponding mathematical relationships. Along with the causes discussed earlier [7], this situates contributes markedly to the ambiguity of experimental data interpretation within a geometric–probabilistic scheme.

To restore the balance, the inherent deterministic chemical aspects of locality need to be represented within the formal description irrespective of (i.e. separately from) energetic inhomogeneity. In this respect, the appropriate formal description must be attributed to the original solid reagent treated as a chemical individual. This may be done in terms of planigons using the approach suggested earlier [8].

2. Model two-dimensional planigon representation versus real three-dimensional reaction interface

The use of planigons for representing the chemical individuality of a solid reagent in mathematical models was introduced earlier, proceeding mainly from the intrinsic logic of the geometric–probabilistic formalism [7–9]. However, even a passing glance at any scanning electron micrographs, which are not infrequently included in experimental studies on solid-phase reaction kinetics and mechanism (e.g. [4,10]), may well throw doubt on this intrinsic logic. Actually, the real reaction interface is essentially three-dimensional [11,12], and quite different events may well occur in the various parts of its bulk. Accordingly, the question arises: what exactly is represented in terms of 2D planigons in this complicated 3D picture?

This question forms part of a more general question: what exactly is described when solid-phase reaction kinetics, e.g. thermal decomposition kinetics, are simulated by the widely used Avrami–Erofe'ev equation

$$\alpha(t) = 1 - e^{-kt^n} \tag{1}$$

or some other similar geometric–probabilistic equation in terms of the degree of conversion α. The usual answer is that this equation formally describes the formation and growth of new phase nuclei due to some chemical and related physical processes. If this is so, however, there is no room for representing the original solid reagent within the formalization. Furthermore, one cannot talk about representing it as a chemical individual. The contradiction is especially obvious when only gaseous products are formed, e.g. $2HgO \rightarrow 2Hg + O_2$.

Hence any correct formal description must represent the formation of one or other product as the consequence of such bond redistributions as leads to the disappearance of the initial crystal structure. We will here term this process "the growth of a negative crystal", noting that this term may have slightly different meanings in other contexts. From a formal viewpoint the geometric–probabilistic scheme is adequate for describing the origination and growth of negative crystals as well as conventional nuclei. But one and the same equation cannot be used for simultaneous simulation of both these processes, apart from infrequent cases of complete coherence of all steps. In this way we arrive at the necessity of separating the negative crystal growth within a geometric–probabilistic description of solid-phase reaction kinetics. An original single crystal with a surface we will represent as a substrate, possessing 3D periodic structure, with several atomic layers at the "selvedge" [13]. Even outside of a reaction the selvedge may differ materially from the substrate, e.g. in the symmetry (reconstruction). But it is still symmetrical, and it is this 2D periodicity which is represented by planigons in the framework of the suggested approach.

The thermal decomposition of NH_4HCO_3 provides a suitable illustration of this point [12]: clearly observed regular (rhomboid on (001) face) thermal decomposition structures, which are the negative crystals of the original phase, are filled by the porous product.

Characterizing the reaction kinetics with some indirect integral measurement, e.g. thermal effects, to be compared with the calculated $\alpha(t)$ curve, and then attributing these measurements to the new phase formation alone, one will make an obvious mistake. One may estimate this mistake, for example, from the error obtained by comparing the heat of formation of oxides with the heat of oxygen chemisorption on the corresponding metals proceeding without rupture of the crystal lattices [14].

In previous articles [7–9] the main arguments in favor of a two-dimensional approach were connected mainly with mathematical considerations: the independence of the geometric–probabilistic models from their dimensionality and the possibility of making more explicit the inherent nature of IKP ambiguity in two dimensions; the intention to give up the spherical form of nuclei; the possibility of using the logic of measure assignment in the IKP structure, etc. The separate description of negative crystal growth in the selvedge of the original solid reagent introduces more ponderable arguments connected with symmetry considerations.

3. Symmetry insight into the problem

A phenomenon can hardly be considered as being completely understood until the particular interrelations between the symmetry of causes and the symmetry of effects are manifested, the general principles having been formulated by Curie [15]. The forms of spot localization were compared with crystal symmetry by Kohlschütter [16]. The experience accumulated since then shows that, if an original crystal is prepared carefully and a reaction is carried out under conditions required for the kinetic regime, this symmetry correspondence is as a rule observed [12].

Note that one and the same object may be considered in terms of symmetry as an individual or as a medium, depending on circumstances [17]. For negative crystal growth the original single crystal thus plays the role of the medium. In crystal chemistry the geometric model of a crystal, which is the limiting simplification of its physical model, if considered irrespective of basic principles of thermodynamics, solid-state physics and quantum mechanics, provides in many cases a sufficient understanding of its structure and symmetry [18]. With this in mind, it seems possible and expedient also to represent the advance of the reaction front in terms of symmetry and irrespective (at this stage) of the particular nature of a reaction.

The suggested 2D representation in terms of planigons emphasizes essential distinctions in interface advance along the selvedge and into the bulk. Some material arguments of fairly disparate nature in favor of this 2D representation, connected with symmetry considerations, may be pointed out.

(i) First of all, there is much experimental evidence (e.g. [12,19]) that the same reaction may proceed in different ways on the different faces of the same crystal, and that different chemical processes on the same crystal face may be characterized by different localization forms.

(ii) When a real single crystal grows from a nucleus, each of its faces advances (preserving orientation) in one direction. As a result the normal to a face of a real crystal is always geometrically polar, and not infrequently a real crystal is considered as the aggregate of growth pyramids [17]. The existence of geometrical polarity means that some other properties may be polar, thus indicating another material aspect of the disequivalence of directions.

(iii) The geometric–probabilistic formalism is independent of the dimensionality, and it was noted earlier [7] that a number of misinterpretations may be connected with this. One of them concerns the discussed point. If the growth of 3D nuclei is considered, their appearance must occur uniformly all over the volume to be filled ultimately by a new phase (Fig. 1(a)). Otherwise the applicability conditions discussed in [7] will not be satisfied. If the nuclei appear at a surface only (Fig. 1(b)) these conditions require that they grow in two dimensions. By assuming in this case three-dimensional growth (Fig. 1(c)), one arrives at the contradiction that formation of nuclei is no longer according to Poisson from the viewpoint of their subsequent growth. At the same time the real solid-phase reactions correspond just to this combination of 2D nuclei formation and 3D nuclei growth, which thus may be formalized rigorously in the framework of the geometric–probabilistic scheme only in the form of a "layered" model (Fig. 1(d)).

Hence it follows from both chemical and mathematical considerations that, in simulating negative crystal growth, the reaction front advance along the surface and into the bulk must be formalized separately within the geometric–probabilistic approach. The representation of a single crystal with a surface as a system of parallel crystallographic planes [20] is adequate for this. Following this logic, it is reasonable to associate the advance of the reaction front first of all with the translational symmetry.

4. Reaction front advance in terms of Wigner–Seitz cells

The structure of a real essentially inhomogeneous surface is determined not only by general energetic considerations but also by particular growth processes (his-

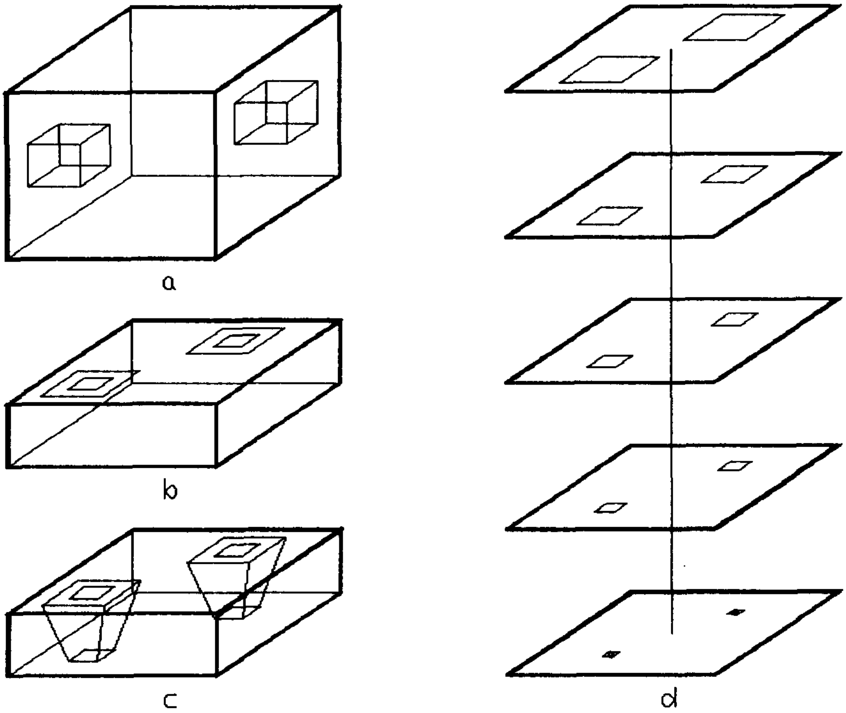

Fig. 1. The conventional geometric–probabilistic description assumes the same dimensionality of nuclei formation and growth (a), (b); otherwise (c) the "layered" representation (d) is required.

tory), deterministic chemical regularities of the reaction front advance being masked by the latter. The model suggested [8] takes this into account through superimposing two types of Dirichlet domains: the random mosaic characterizes the surface inhomogeneity, whereas planigons represent its symmetry. It is worth emphasizing once again that, whereas origination of a reaction is determined mainly by energetic inhomogeneity, its further evolution is connected largely with the crystal chemical structure of a reagent. Aiming to separate the latter within the formal description, we will consider here the origination and 2D growth of one negative crystal in the initially homogeneous selvedge.

The appearance of a nucleus means in this context the significant enhancement of the ease of bond rearrangement steps in its nearest vicinity. When talking in [8] about "transmission (or propagation) of an interaction from one planigon to another" we actually left this term without explanation. Further, it will denote a significant increase in the probability for the given center of action to participate in the elementary single-barrier event provided that the neighboring center of action has entered the reaction. One direct illustration of this is the regular periodic change of the electron density distribution as a result of gas chemisorption on metal surfaces [21]: the one-center chemisorption results in the weakening of bonds between the given chemisorption center and the neighboring surface atoms, and in the simultaneous strengthening of bonds with subsequent atoms ("second surroundings"). The electron density redistribution may be considerable, up to the removal of the metal atom from the surface. Note also an interesting example of localization when partial adsorption of hydrogen on a silicon surface results in the appearance of "surface drops" of (1 × 1) structure within the unchanged (2 × 1) superstructure [22].

Everything that has true value in chemistry is connected in one or another way with the electronic structure of atoms and molecules [23]. In the context of the up-to-date formalism of solid-phase reaction kinetics, this phrase is seldom heard. It is worth noting in this connection that planigons represent the symmetry of not only atomic nuclei positions but also the time averaged 2D cross-sections of electron density distribution [18]. This raises the hope that, in the long run, the above quote will be uttered quite routinely. Along with the one-to-one correspondence between planigons and two-dimensional Fedorov groups, this determines the central role of planigons in the suggested approach and the use of Wigner–Seitz cells for representing the advance of the reaction front.

The complete mathematical theory of planigons was developed in [24]. Planigons are independent (fundamental) regions of corresponding symmetry groups. We will deal with a particular case of planigons, i.e. Dirichlet domains for surface atoms belonging to the same regular system of points (system of equivalent positions, or orbit). Although sometimes symmetrical by form, planigons are essentially asymmetrical in the sense that their internal points are not interconnected by symmetry operations, symmetry elements being situated only at the planigon boundaries. Each regular system is represented by one surface atom inside a planigon. The "propagation of an interaction" responsible for the reaction front advance is determined by the translational structure of a surface. This structure is characterized completely by Wigner–Seitz cells, which are also Dirichlet domains but constructed for translationally equivalent lattice points alone [25]. A Wigner–Seitz cell is an elementary cell of a crystal structure possessing the symmetry of the corresponding Bravais lattice. Each type of translationally non-equivalent lattice points is represented by one point in a Wigner–Seitz cell, which is always centrosymmetric and may be either a quadrangle or a hexagon.

In these basically geometrical terms the above considerations may be formalized as follows.

The simplest case for describing the unrestricted growth of a 2D negative crystal is the P1 symmetry group, containing only translations. It is represented by two planigons (Fig. 2): one quadrangle and one hexagon [24]. In our context, the important distinguishing feature of this group is that the same polygons are also Wigner–Seitz cells (and at the same time parallelogons [18]). It is this simplest case that was assumed previously [8]. It enables one to emphasize the following material point, namely that an object may possess different symmetry in different respects [17]. Planigons represent the symmetry of infinite 2D crystal structure P1. In this respect the planigon is asymmetric, i.e. its center of action (marked in Fig. 2 with an asterisk) is not the symmetry center of the given planigon. We are interested in the growth of a finite symmetrical figure (negative crystal) possessing at least a

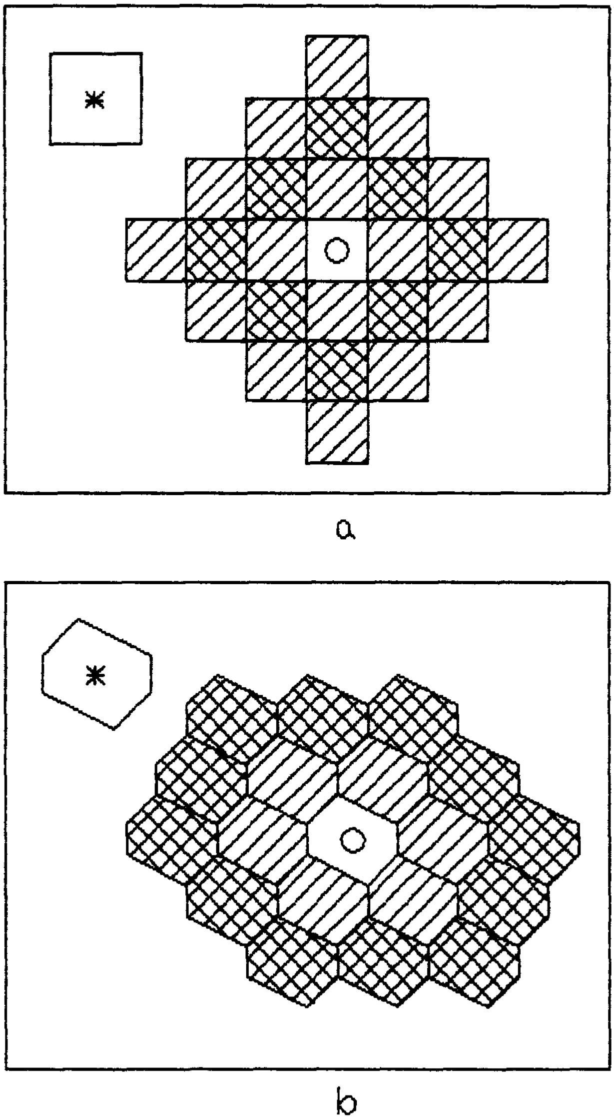

Fig. 2. Two possible types of unrestricted growth in the simplest case of the P1 symmetry group; different hatching shows the sequential "entry of planigons into reaction".

symmetry center. At this point, it is important that for the P1 symmetry group the same polygon represents a centrally symmetric Wigner–Seitz cell. (We will see below that this is not the case for other symmetry groups). It is thus the treated symmetry center that serves as the center of the growing negative crystal.

Consideration of the next symmetry group P2 allows one to discuss practically all major aspects concerning interrelations between planigons, Wigner–Seitz cells and

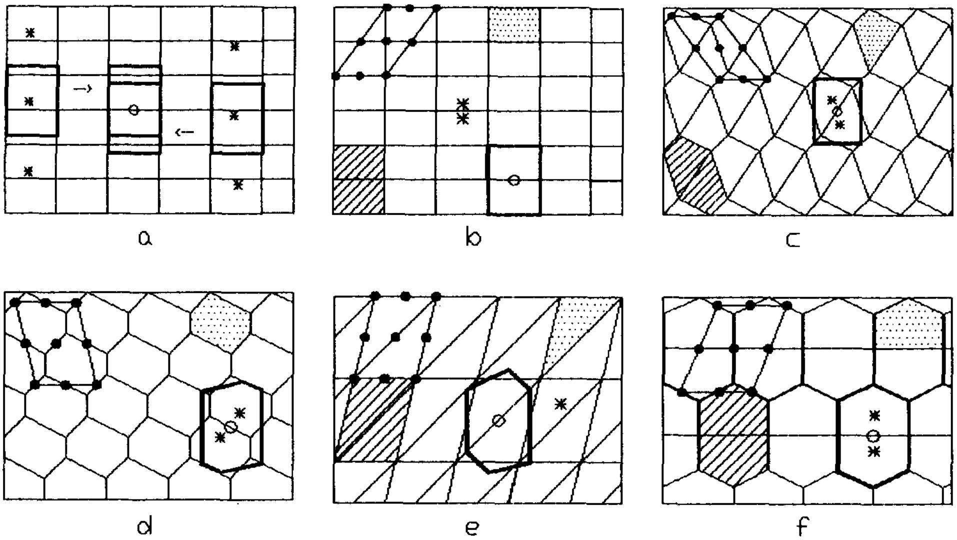

Fig. 3. All possible interrelations between planigons (dotted hatching), Wigner–Seitz cells (heavy lines) and parallelogons (line hatching) for the P2 symmetry group. Centers of action are shown for planigons by asterisks and for Wigner–Seitz cells by empty circles; filled circles denote two symmetry axes and are shown for conventional elementary cells.

parallelogons in simulating the advance of the reaction front (Fig. 3). Generally a planigon has 3–6 edges, and the P2 symmetry group is represented by all possible polygons, quadrangles being presented in two variants [24].

The picture differs essentially even in the case of "similar" quadrangles and hexagons (Fig. 3(b), (d)): now the planigons possess symmetry axes at the boundary, and each Wigner–Seitz cell contains two translationally non-equivalent lattice points. Although the considered planigon $D_{4A,8}$ (keeping here the notation from [24]) is centrosymmetric in form, its center cannot serve in this case as the center of a growing negative crystal. To find the appropriate center, one has to construct Wigner–Seitz cells for each of two translationally non-equivalent points. Their intersection will also be centrally symmetrical (Fig. 3(a)), this center being the center for the growing negative crystal. In this simplest case two planigons are united into a parallelogon coinciding with the Wigner–Seitz cell (Fig. 3(b)). But even in the case of another quadrangle, $D_{4A,1}$, the corresponding parallelogon is a hexagon, the Wigner–Seitz cell is a rectangle, and the conventional elementary cell is a parallelogram (Fig. 3(c)). This means that the hexagonal parallelogon will be translated in this case in four rather than in six directions from the center determined as described above.

In the case of the $D_{6,4}$ planigon (Fig. 3(d)) the Wigner–Seitz cell is a hexagon covering two translationally nonequivalent planigons which do not in total form a parallelogon. The similar Wigner–Seitz cell in the case of the $D_{3A,3}$ planigon (Fig. 3(e)) unites two planigons into a parallelogon which is a parallelogram. Finally, two pentagonal planigons $D_{5A,1}$ (Fig. 3(f)) are united into a parallelogon coinciding with a hexagonal Wigner–Seitz cell.

Further, a diagram similar to that in Fig. 2 may be constructed for each of Fig. 3(b)–3(f), representing the reaction front advance. Each Wigner–Seitz cell in this diagram will contain planigons (according to Fig. 3) determining particular localization forms.

The above examples enable one to state the following general scheme. For simulating the 2D reaction front advance in terms of planigons and Wigner–Seitz cells one has to do the following.

(i) Construct the Wigner–Seitz cell for an arbitrary point of the considered lattice; this cell will contain some translationally non-equivalent points.

(ii) Construct the Wigner–Seitz cells for each of these points; the intersection of these cells will be centrally symmetrical, and this symmetry center is the center of the growing negative crystal.

(iii) Construct around this center a diagram (consisting of quadrangle or hexagonal Wigner–Seitz cells) similar to that in Fig. 2.

(iv) Place planigons into each Wigner–Seitz cell for determining the localization form.

This geometrical construction may be made for any symmetry group and then may be included in a more general scheme [7,8] taking account of the probabilistic part of the problem.

5. Conclusions

Therefore, in considering the interconnections

$$\begin{array}{ccccc} & & \text{localization} & & \\ \text{chemical} & \rightleftarrows & \text{of a solid-phase} & \rightleftarrows & \text{geometric-probabilistic} \\ \text{interpretation} & & \text{chemical reaction} & & \text{description} \end{array}$$

one arrives at the necessity of attributing the geometric– probabilistic description first of all to the original reagent in the form of a single crystal, three main subsequent steps being involved.

(i) Separate the negative crystal growth.

(ii) Separate the 2D description of the reaction front advance along the surface.

(iii) Represent this by an account of the translational symmetry of a surface.

The simultaneous use of two varieties of Dirichlet domains, planigons and Wigner–Seitz cells, makes more precise the deterministic part of the approach suggested in [8] and determines the peculiarities of the geometrical part of the geometric–probabilistic formalism connected with localization phenomena.

Because the inhomogeneity of the original solid reagent is not taken into account at this stage, symmetry considerations become efficient, and the most convincing arguments in favor of the essentially 2D approach suggested are based mainly on these considerations. At the same time it becomes clear how the sample inhomogeneity may be taken into account and a 3D picture may be constructed from 2D "layers".

In mathematical terms, we restrict ourselves here to a geometrical presentation alone for emphasizing mainly conceptual aspects. To include this in the IKP structure necessitates alternative algebraic formalization in terms of difference equations taking account of the discrete character of the approach. This point merits separate discussion and will be the subject of a subsequent paper.

Acknowledgments

This work was undertaken in the Laboratory of Molecular Dynamics and Structure, Kharkov University. I thank Professor I.V. Krivoshey for his encouragement.

References

[1] J. Šesták, Thermophysical Properties of Solids, Their Measurements and Theoretical Thermal Analysis, Elsevier, Amsterdam, 1984.

[2] M.E. Brown, D. Dollimore and A.K. Galwey, Reactions in the Solid State, Elsevier, Amsterdam, 1980.

[3] P. Barret, Cinétique Hétérogène, Gauthier-Villars, Paris, 1973.

[4] B. Delmon, Introduction à la Cinétique Hétérogène, Éditions Technip, Paris, 1969.

[5] V.Z. Belen'kiy, Geometric-Probabilistic Models of Crystallization, Nauka, Moscow, 1980 (in Russian).

[6] I. Langmuir, J. Am. Chem. Soc., 38 (1916) 2221.

[7] A. Korobov, Thermochim. Acta, 243 (1994) 79.

[8] A. Korobov, Thermochim. Acta, 224 (1993) 281.

[9] A. Korobov, J. Therm. Anal., 39 (1993) 1451.

[10] A.K. Galwey and M.A. Mohamed, Thermochim. Acta, 213 (1993) 279.

[11] A.K. Galwey, J. Therm. Anal., 38 (1992) 99.

[12] E.A. Prodan, Topochemistry of Crystals, Nauka i Tekhnika, Minsk, 1990 (in Russian).

[13] D.P. Woodraff and T.A. Delchar, Modern Techniques of Surface Science, Cambridge University Press, Cambridge, UK, 1968.

[14] J.Bérnard (Ed.), Oxydation des Metaux, Gauthier-Villars, Paris, 1962.

[15] P. Curie, J. Phys., 3 (1894) 939.

[16] V. Kohlschütter and M. Lüthi, Helv. Chim. Acta, 13 (1930) 978.

[17] A.V. Shubnikov, Selected Papers on Crystallography, Nauka, Moscow, 1975 (in Russian).

[18] B.K. Vainshtein (Ed.), Modern Crystallography, Vol. 1, Nauka, Moscow, 1979 (in Russian).

[19] E.A. Prodan, J. Therm. Anal., 29 (1984) 941.

[20] F.Bechstedt and R. Enderlein, Semiconductor Surfaces and Interfaces, Their Atomic and Electronic Structures, Akademie-Verlag, Berlin, 1988.

[21] H. Dunken and V. Lygin, Quantenchemie der Adsorption an Festkörperoberflachen, VEB Deutscher Verlag für Grundstoffindustrie, Leipzig, 1978.

[22] W.A. Harrison, Electronic Structure and Properties of Solids, W.H. Freeman and Co., San Francisco, CA, 1980.

[23] I. Hargittai and M. Hargittai, Symmetry Through the Eyes of a Chemist, VCH Verlagsgesellschaft, Weinheim, 1986.

[24] B.N. Delaunay, N.P. Dolbilin and M.P. Shtogrin, Proc. Math. Inst. Acad. Sci. SSSR, 148 (1978) 109 (in Russian).

[25] E. Wigner and F. Seitz, Phys. Rev., 43 (1934) 804; 46 (1934) 509.