SIMULATION OF THE ADVANCE VELOCITIES OF STEPS OF DIFFERENT CRYSTALLOGRAPHIC DIRECTIONS ON THE (110) FACE OF YTTRIUM IRON GARNET: THEORY AND OBSERVATIONS

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Abstract. During the Oji seminar a poster was presented resulting from international cooperation between three research groups. The theory behind this poster and the results are now presented in detail.

In the first part a summary of an integrated approach of a network analysis based on the morphological theory of Hartman and Perdok and statistical mechanical Ising models is presented. This theory was applied to explain faces occurring on garnet crystals and forms a basis for modelling of advance velocities of steps with different crystallographic directions to be presented in the next part. Conditions are discussed under which the results of this theory can be employed for the kinetic sublattice model. The concept of kinks is discussed. The structure of the slice (022)\(_1\) is analysed. Also the way two adjacent slices of (022)\(_1\) faces are connected to each other is described.

In the second part a kinetic sublattice model is developed, which yields a set of coupled differential equations providing the possibility to calculate the advance velocities of steps with different crystallographic directions in dependence of supersaturation. This theory is then applied to steps on the (022)\(_1\) slice. The concept of kink which is well defined for simple Kossel-like crystals is now generalized for such complex crystal slices as those of garnet. Expressions are derived for the surface free energy from the developed kinetic equations.

In the third part using the kinetical sublattice model of Part 2 the advance velocities of steps of different crystallographic directions on the (022)\(_1\) slices of
YIG are calculated in dependence on the supersaturation. Calculated and observed ratios of rates of growth in different crystallographic directions are in good agreement with each other. Also the observed phenomenon of interlaced step-patterns is explained. The concept of waiting time is introduced which determines time intervals between successive elementary events for the growth units of different kinds to enter the crystal lattice during the growth process. The dependence of waiting times and the width of steps in dependence on supersaturation is also discussed.

It is calculated for which ratio's and values of bond energies and ratio's of frequency factors observed and calculated anisotropies in the advance velocities of steps on the (011) face of YIG can be matched within an accuracy of one percent.

PART 1

1.1 Introduction

In this first part of our paper we will summarize the results of a geometrical or topological network analysis of the slice (022)₁ or connected nets of garnet.¹ We will extend the topological work of Ref. (1) by discussing not only the structure of the connected nets, but also the system of bonds between adjacent connected nets. This part will give the necessary geometrical basis for a statistical mechanical sublattice model to be presented in the second part.

The formalism of this sublattice model will allow us to calculate by computer the advance velocities of steps with different crystallographic orientations in dependence on the supersaturation. The results of the computer calculations will subsequently be compared with observed ratio's of advance velocities of steps with different crystallographic orientations. This will be the subject of the third part.

1.2 Structure and Systems of Bonds of Garnet

Before discussing the structure of (022)₁ slices or connected nets, which will form the basis of Parts 2 and 3 we will summarize the most relevant data of garnet and related subjects as published in recent papers.¹,³

The general formula for garnet is given by

\[ \text{C}_3\text{A}_2\text{D}_3\text{O}_{12}. \]  \hspace{1cm} (1.1)

There are two groups of garnets, namely:

(i) natural garnets where D stands for the tetravalent Si⁴⁺ ion, A for
threevalent ions such as Al\(^{3+}\) or Fe\(^{3+}\) etc. and C for divalent ions such as Ca\(^{2+}\) of Mg\(^{2+}\) etc.,

(ii) synthetic garnets where all ions C, A and D are trivalent. Here A and D are for example Fe\(^{3+}\) and C for example Y\(^{3+}\) or rare earth ions.

One of the most well-known synthetic garnets is YIG (Yttrium Iron Garnet) \(Y_3Fe_5O_{12}\). In the following we will focus our attention on YIG. We note that C ions correspond to dodecahedral sites and are surrounded by eight O ions, A ions correspond to octahedral sites and are surrounded by six O ions and D ions correspond to tetrahedral sites and are surrounded by four O ions. In one unit cell there are 24 D and C ions, 16 A ions and 96 oxygen ions. The whole structure consists of coupled dodecahedra, octahedra and tetrahedra with C, A and D ions in the centre and O ions at the corners. These polyhedra share edges or corners. In case of YIG Fe\(^{3+}\) ions are situated on D and A sites and Y\(^{3+}\) on C sites.

The garnet structure is described by the cubic space group \(I4_1/a\bar{3}2/d\). The elementary cell parameter is about 13 Å.\(^1\) It can immediately be seen from a structural model, that if only first nearest neighbour bonds between positive and negative ions are taken into consideration the whole structure consists of coupled tetrahedra with one oxygen ion in the centre and the D, A and two C ions at the corner (see Fig. 1.1).

In this tetrahedron description, four first neighbour bonds D, A and two times C are defined. Following Refs. (1, 2) we consider \(\phi_D\), \(\phi_A\) and \(\phi_C\) as bond energies consisting of sf (solid-fluid), ss (solid-solid) and ff (fluid-fluid) bonds. As an example we write for the bond energy \(\phi_D\) corresponding to a D-bond

\[
\phi_D = \phi_D^{sf} - \frac{1}{2} (\phi_D^{ss} + \phi_D^{ff}).
\]

It is shown in Ref. (1) that 10 different \(F\) slices could be derived for garnet. An \(F\) slice is defined as a two dimensional connected net of ions. It must be possible to divide the whole structure unambiguously into the same connected nets.\(^4\),\(^5\) The overall interplanar thickness of the nets is \(d_{nnnhnn}\) where \(n\) may be larger than unity due to the extinction conditions of the space group. In order to disconnect such a connected net, bonds have to be cut along two different crystallographic directions. A crystallographic plane parallel to such a net will in principle grow by a layer mechanism, i.e. a spiral growth mechanism or a two dimensional nucleation mechanism, provided the actual dimensionless temperature \(\theta=2kT/\phi_D\) is smaller than the dimensionless roughening temperature \(\theta^K=(2kT/\phi_D)^K\). The best criterion to characterize the roughening temperature is to use \(\theta^K\), which corresponds to a roughening transition of the so-called solid on solid (SOS) model. The character of this roughening transition has been clarified in recent years on basis of the so-called XY model. For complex nets we cannot find \(\theta^K\) and instead of this we use \(\theta^C\) which
corresponds to the critical temperature for the order-disorder phase transition in a two-dimensional connected net according to the theory of Onsager. It has been shown that $\theta^K$ and $\theta^C$ are close to each other for simple nets. It is shown that the calculated orders of dimensionless Ising temperature $\theta^C$ give an order of morphological importance of crystal faces which is in good agreement with a large variety of experimental data.\(^1\) For the theory of connected nets, roughening transition and the connection with the order-disorder phase transition of Onsager we refer to Refs. (3, 4, 5).

In Ref. (1) the 10 $F$ slices are simplified using two logically straightforward recipes which are (i) attached ions are removed, (ii) an alternative garnet structure and accompanying bond structure are used. Here attached ions are ions which are just at the boundary of two adjacent $F$ slices. They belong statistically spoken with a weight of one half to a slice (see also Ref. (5)).

In Ref. (2) a statistical mechanical formalism was developed to transform the structure and system of bonds of tetrahedra (Fig. 1.1) into an oxygen-free structure with a system of cation-cation bonds coinciding with the edges of the tetrahedron (Fig. 1.2) and a four-point interaction energy. It was shown also in Ref (3) that this interaction when compared to the two-point one, may be neglected. The developed spin Hamiltonian formalism gives a deeper physical meaning to the usual broken bond conventions used in the Hartman Perdok theory which enables us to construct boundaries of connected nets or $F$-slices.\(^4\) Breaking a cation-cation bond means to replace one solid cation ion by an average fluid ion of the mother phase. This corresponds to changing the spin from a spin up to a spin down.

1.3 Geometrical Basis for the Sublattice Model

We will base the statistical mechanical formalism to be presented in the next part on the combined result of the network analysis of garnet and the

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**Fig. 1.1**  
D, A and C bonds with a tetrahedron in the real garnet structure.

**Fig. 1.2**  
AD, two CD, two CA and CC bonds in tetrahedron of oxygen-free garnet structure.
star-tetrahedron transformation or tetrahedron model of Ref. (2) (see Figs. 1.1 and 1.2). Using our physical intuition this means that we consider the growth units as average growth units of cations to which oxygen ions are attached with a certain statistical weight. This idea was already discussed in Refs. (2, 1). It was shown, that in the extreme case of a complete association D model, where D bonds are much stronger than other bonds, all oxygen ions belong to DO₄ tetrahedra and these are then the growth units, which enter the crystal lattice. Thus D bonds do not play a role in the crystallization process nor do they contribute to the enthalpy of dissolution. So in the following we assume that for the simplified crystal structure of garnet we have to do with a lattice of D, A and C ions and their interaction is characterized by the effective bond energies $\phi_{AD}, \phi_{CD}, \phi_{AC}, \phi_{CC}$. For the time being we will neglect the weak and negative fourpoint interaction energy $\phi_{DACC}$. As discussed in Ref. (3) this is justified.

The next presupposition in our approach to be developed below is, that we base our calculations on the simplified $F$ slices as presented in Ref. (1), which means that we remove the attached ions. We assume that both for thermodynamic equilibrium and the growth processes the characteristic times of elementary events of attached ions are much lower than the characteristic times determining equilibrium and growth of a basic slice. So we assume that attached ions do not play an essential role in the formation of the basic structure and the strength of an $F$ slice. Hence they can be removed. This implies that depending on the composition of base and boundary of a particular $F$ slice, each basic $F$ slice will have a different non stoichiometric composition and different structure. So far we used the arguments, which are valid for a crystal in equilibrium with its saturated motherphase. If we want to carry out kinetic calculations on a basic $F$ slice without attached ions we assume in fact that the rate determining step is a layer growth mechanism of the basic $F$ slice. This can be justified in the following way. It follows from Ref. (1) that an $F$ slice of garnet consists of a basic $F$ slice with a $\theta$ factor smaller than $\theta^C$ and an attached slice of an $S$ or $K$ character, with an $\theta^C=0$ (for a definition of $S$ and $K$ faces, as used in the Hartman Perdok theory, see Ref. (6)). So the attached slice grows with a kind of continuous mechanism, which is much faster than a layer growth mechanism. We cannot immediately apply these simple concepts to the growth of complex garnet slices, since the growth of the basic slice and the attached slice are coupled. We will assume, however, that we may neglect in our kinetic growth equations the attached ions and again base our calculations on the basic $F$ slices without attached ions (see also Ref. (5)).

It was shown in Ref. (1) that quite often two alternative $F$ slices could be identified for the same crystallographic plane. In this and next parts we will investigate the (022) face, because this is the strongest connected net and will certainly dominate the crystal growth form (see Refs. (1–3, 5)).
It has been shown in Refs. (8–11) that volume diffusion and surface diffusion play a role in the growth process of YIG crystals growing from a supersaturated PbO flux. The step integration, however, is to a high extent rate determining. This is also in agreement with the anisotropy in growth rates of steps with the different crystallographic orientations (see Part 3 and Ref. (1)). We will assume in this Chapter that step integration is (absolutely) rate determining.

It follows from the considerations given above that the formalism of the kinetic sublattice model is based on the following presuppositions.

(i) Only first nearest neighbour bonds are taken into consideration.

(ii) The system of first nearest neighbour bonds is transformed in the system of cation–cation bonds using the so-called star tetrahedron transformation and neglecting the four point energy.

(iii) Attached ions are removed from the connected nets and it is assumed that the formation of a basic slice is rate determining.

(iv) The attachment of ions to the steps is rate determining in the growth process.

In passing we note, that the problem how to calculate for the boundary YIG–PbO bond energies will be treated in the third part.

1.4 Kink Sites

It is well-known, that in crystal growth models based on simple Kossel-like crystals the kinks play an essential role for the definition of equilibrium conditions.\(^7\) This also especially holds true for computer simulations of Ising-like models. For more complex Ising-like crystal models of garnet the concept of kinks has to be generalized. Taking into consideration the bulk of the oxygen-free first neighbour tetrahedron model of garnet, kinks can be unambiguously defined. It is shown in Ref. (1) that the following bonds originate from respectively

\[
\begin{align*}
D: & \quad 4AD, \quad 8CD \\
A: & \quad 6AD, \quad 12AC \\
C: & \quad 8CD, \quad 8AC, \quad 8CC.
\end{align*}
\]

(1.3)

So the kink energies are respectively

\[
\begin{align*}
K_D &= 2\phi_{AD} + 4\phi_{CD} \\
K_A &= 3\phi_{AD} + 6\phi_{AC} \\
K_C &= 4\phi_{CD} + 4\phi_{AC} + 4\phi_{CC}.
\end{align*}
\]

(1.4)

In case of the reduced slices a part of the ions and their bonds in (3), (4) are
removed. So for each basic \( F \) slice "kinks" have to be defined. Ions in these kink positions will have lower bond energies than ions in the real kinks. In Part 2 we will come back to the problem of kinks where a general statistical mechanical treatment of this problem will be given.

1.5 Basic \((022)\); Slice

In Figs. 1.3(a) and (b) we have given the schematic basic \( F \) slices of the \( F \) slice \((022)\). It also can be seen from Figs. 1.3(a) and (b) how a higher slice (Fig. 1.3(b)) is oriented in reference to a lower slice (Fig. 1.3(a)). Since the stacking is complex and since for our formalism the interaction of ions between slices has some importance, we have schematized the interaction between the ions in four sectors (Figs. 1.3(c), (d), (e) and (f)). The sectors 1, 2, 3, 4 are indicated in Figs. 1.3(a) and (b). With these figures the configurations speak for themselves. The bonds between the cations are indicated as \( \phi_{AD}, \phi_{CA} \) and \( \phi_{CD} \) etc. We note that sometimes double bonds occur.

It can be seen from Figs. 1.3(a)–(f) that for the connected net \((022)\), the first nearest neighbours of A, D and C ions are respectively 2C and 2D; 2A and 1.5C; 2A, 1.5D and 0.5C respectively.

PART 2

2.1 Introduction

In a series of previous papers\(^{11} - ^{13}\) a theory yielding kinetic equations has been developed for the growth of multicomponent crystals. The applicability of these kinetic equations obtained from a one- and two-partition approximation of the distribution function as well as from mean field approximation has been thoroughly studied. Models based on one lattice and on sublattices have been developed. It was shown that the growth of ordered multicomponent crystals and chemical compounds is adequately described in terms of sublattices. According to this, a generalized kinetic Ising model of a lattice gas will be used to investigate the growth kinetics of garnet crystals.

According to the models of connected nets described in a previous paper\(^1\) and Part 1 above, the growth units—the ions A, D and C—occupy in a crystal the cells of given sublattices forming altogether a simplified crystallographic lattice of garnet. A liquid cell is characterized by the average properties of the liquid phase,—such as, for example, composition, heat of mixing, configurational part of entropy, etc.
FIG. 1.3(a). Connected net of the (022) slice.

FIG. 1.3(b). Connected net of (022); one layer higher (or lower) as compared to Fig. 1.3(a).
Fig. 1.3(c). Vertical cut according to sector 1. See Figs. 1.3(a) and (b).

Fig. 1.3(d). Vertical cut according to sector 2. See Figs. 1.3(a) and (b).

Fig. 1.3(e). Vertical cut according to sector 3. See Figs. 1.3(a) and (b).

Fig. 1.3(f). Vertical cut according to sector 4. See Figs. 1.3(a) and (b).
2.2 Elementary Event Probabilities

The number of first neighbours as defined in Section 1.5 will serve as starting point to determine the elementary event probabilities for attachment and detachment of particles on the surface. In the following we present the detachment probability per time unit for a particle of the \( \nu \)-kind (where \( \nu = A, C, D \)) in the form:

\[
W_{01}^{\nu} = \Omega_\nu \exp \left[ -\sum_{\gamma=A, D, C} \frac{I_{\nu\gamma} \phi_{\nu\gamma}}{kT} + \theta_\nu \right].
\] (2.1)

Here the index 1 denotes that a particle of a given kind belongs to the solid phase, and the index 0—that it belongs to the liquid phase.

It has already been noted in Part 1 that we restrict ourselves to pair interactions of the nearest neighbour particles in the crystal only. In Eq. (2.1) the symbol \( I_{\nu\gamma} \) denotes the number of \( \nu \)-ions with nearest neighbours of solid \( \gamma \)-particles on the surface, belonging to a crystal in the neighbourhood of the lattice cell, where the \( \nu \)-particle is supposed to be exposed to the elementary event. The frequency factor \( \Omega_\nu = W_\nu \exp (-U_\nu/kT) \) is determined by the characteristic vibration frequencies \( W_\nu \) of \( \nu \)-particles in the liquid phase, and the activation energies of their attachment to a crystal \( U_\nu \). The frequency of an elementary attachment event is given by

\[
W_{10}^{\nu} = \Omega_\nu \exp \left( \frac{\Delta\mu_\nu}{kT} \right).
\] (2.2)

Here \( \Delta\mu_\nu/kT \) is the supersaturation of the \( \nu \)-particles in solution. The parameters \( \theta_\nu \) are found from the condition that for the kink-site position at the crystal face the following relation holds true

\[
\left[ \frac{W_{10}^{\nu}}{W_{01}^{\nu}} \right]_{\text{kink}} = \exp \left( \frac{\Delta\mu_\nu}{kT} \right).
\] (2.3)

It can be seen that for \( \Delta\mu_\nu = 0 \), i.e. for thermodynamic equilibrium, \( (W_{10}^{\nu})_{\text{kink}} = (W_{01}^{\nu})_{\text{kink}} \) in agreement with the properties of a kink. So the kink concept of a simple Kossel-like crystal is now generalized. For more complex crystals we have more than one different kinks (Halbkristallage). From Fig. 1.3 of Part 1 it can be seen that for the slice \((022)\)

\[
\theta_A = \frac{2\phi_{AD} + 2\phi_{AC}}{kT}; \quad \theta_D = \frac{2\phi_{AD} + 2.5\phi_{CD}}{kT};
\]

\[
\theta_C = \frac{2\phi_{AC} + 2.5\phi_{CD} + 0.5\phi_{CC}}{kT};
\] (2.4)
By definition:

\[ \phi_{CD} = \varphi_{CD}; \quad \phi_{AC} = 2\varphi_{AC}; \quad \phi_{CC} = 2\varphi_{CC}; \quad \phi_{AD} = \varphi_{AD}. \] (2.5)

Thus we assume that the step integration is the limiting step of the growth process, and that the growth units A, D and C are formed at the step edge in agreement with the presupposition (iv) of Section 1.3. (Part 1).

2.3 Kinetic Equations for the Sublattice Model

Let us consider that the solid phase cations A, D and C occupy the cells corresponding to the sites of k-sublattices. These sublattices taken together form the basic structure of the F-slice (022)_1 of garnet. In general the number of sublattices may be more than the number of components, i.e. more than three. This means that A-particles occupy k_A-sublattices, D-particles—k_D-sublattices and C-particles—k_C-sublattices, so that k_A + k_D + k_C = k and k_A, k_D, k_C ≥ 1. This point will be discussed in more detail below.

Consider now both the normal (continuous) growth mechanism of (022)_1 faces and the step growth mechanism by straight monomolecular steps advancing on these faces in different crystallographic directions. Let a coordinate axis z be directed either by a normal to the face plane for normal growth, or along the step advance direction for growth by a step growth mechanism. Let us divide the interface into layers of connected nets perpendicular to the advance direction of the interface in case of normal growth and into strips parallel to PBCs in case of step growth. In the following we will use instead of the word “strip” the word “layer”. The position of a layer is determined by the integral value of z, and \(-\infty < z < \infty\). Under normal growth the values of \(z \rightarrow -\infty\) correspond to the crystalline phase and \(z \rightarrow \infty\)—to the liquid phase. For growth by a layer mechanism the values of \(z \rightarrow -\infty\) determine the crystallized layers on the surface, and the values of \(z \rightarrow \infty\)—the layers of the adsorbed liquid phase on the surface. Let \(C_\nu^p(z)\) be the concentration of the \(\nu\)-particles belonging to the solid phase in a sublattice \(p\) in layer \(z\). Also \(\nu = A, D, C,\) and the index \(p\) has the values given by \(1 \leq p \leq k_\nu\). The sublattices of the chemical compound under consideration were chosen so that one sublattice in the solid phase contains only the particles of the same kind. Therefore the concentration of the \(\nu\)-particles of the liquid phase in a sublattice \(p\) of the layer \(z\) is equal to \(1 - C_\nu^p(z)\), and the identification of sublattices is adequately described by the introduction of two parameters \((\nu, p)\). Based on the approach given in Ref. (11–13) a set of kinetic equations describing the crystal growth process can be written in the form:
\[
\Omega^{-1}(C_0^{\text{eq}}) \frac{dC_\gamma^{\text{eq}}(z)}{dt} = \exp \left( \frac{\Delta \mu_\gamma}{kT} \right) \prod_{q,y} \left[ \frac{C_y^{\text{eq}}(z - 1) - C_y^{\text{eq}}(z)}{1 - C_y^{\text{eq}}(z)} \right]^{m_y^{\text{eq}}(z - 1, z)} [1 - C_y^{\text{eq}}(z)] \\
- C_\gamma^{\text{eq}}(z) \prod_{q,y} \left[ \frac{C_y^{\text{eq}}(z) - C_y^{\text{eq}}(z + 1)}{C_y^{\text{eq}}(z)} \right]^{m_y^{\text{eq}}(z + 1, z)} \cdot \exp \left\{ \theta_r \right\} \\
- \sum_{q,y} \left[ (n_y^{\text{eq}}(z) C_y^{\text{eq}}(z) + m_y^{\text{eq}}(z - 1, z) + m_y^{\text{eq}}(z - 2, z) + r_{\gamma}^{\text{eq}} \phi_{\gamma}^{\text{eq}}) \right] \left\{ \gamma = \Lambda, D, C \right\} \quad (1 \leq q \leq k_y) \right).
\]

(2.6)

We assume that the particles in the liquid phase are completely mixed. Also \( n_y^{\text{eq}}(z) \) is the number of cells that are the nearest neighbours to a sublattice cell \((p, v)\) in layer \(z\) and belong to sublattice \((q, \gamma)\) also in layer \(z\); the value \( m_y^{\text{eq}}(z', z) \) denotes the number of cells which are the nearest neighbours to a sublattice cell \((p, v)\) in layer \(z\) and belong to sublattice \((q, \gamma)\) in layer \(z'\); also \( r_{\gamma}^{\text{eq}} \) is the number of \(\gamma\)-particles—the nearest neighbours to a particle of \((p, v)\)-sublattice, they belong to the face on which the step is moving. The quantity \( r_{\gamma}^{\text{eq}} \) is equal to zero for normal crystal growth. From (2.6) it follows, that we are considering the case when the distance between two nearest neighbours does not exceed twice the distance between layers. Also, in (2.6) the value \((C_0^{\text{eq}})\) stands for the equilibrium concentration of the \(v\)-particles in the solution with temperature \(T\). The slice \((022)_{\text{s}}\) has both single and double CD-bonds. Thus for the latter case in Eq. (2.6) and equations below the numbers of bonds for the C- and D-particles must be multiplied by 2.

In deriving Eq. (2.6) we have used a model “without overhangs”. This means that the elementary event of the attachment of a particle or its detachment may take place only in a surface cell. In other words, all the neighbours in layer \(z - 1\) which are neighbours of this surface cell in layer \(z\), will be solid. According to this, the meaning of the terms in Eq. (2.6) is the following. The term in Eq. (2.6), multiplied by \( \exp(\Delta \mu_\gamma/kT) \) determines the probability to find on the surface such a liquid cell of \((p, v)\) kind in layer \(z\), for which in an atomic layer \(z - 1\) all the cells nearest to it belong to a crystal. The expression \([C_y^{\text{eq}}(z - 1) - C_y^{\text{eq}}(z)]/[1 - C_y^{\text{eq}}(z)]\) represents the probability for each bond to find the solid-liquid bond of a liquid cell \((p, v)\) in layer \(z\) and a solid nearest neighbour cell \((q, \gamma)\) in layer \(z - 1\), if the kind of a liquid cell \((p, v)\) is fixed. The complete number of \( m_y^{\text{eq}}(z - 1, z) \) cells \((q, \gamma)\) in layer \(z - 1\) for which a cell of \((p, v)\)-kind belonging to layer \(z\) is the nearest neighbour, is known from the crystallographic structure of garnet. Thus the probability that all the bonds of the liquid cell \((p, v)\) situated in layer \(z\) with the nearest neighbour cells \((q, \gamma)\) in layer \(z - 1\) will be liquid-solid, is equal to
\[
\left[ \frac{C^\theta_p(z) - C^\theta_p(z)}{1 - C^\theta_p(z)} \right] m^\theta_p(z - 1, z).
\]

This expression has to be multiplied by the probability \([1 - C^\theta_p(z)]\) of finding a liquid surface cell \((p, v)\) in layer \(z\). Finally, the positive terms in Eq. (2.6) determine the probability with which a surface liquid cell \((p, v)\) is attached to a crystal. In an analogous way negative terms in Eq. (2.6) determine the probability of detachment of a solid surface cell. We note that previous papers have illustrated that models "with overhangs" give unsatisfactory agreement with the experimental results for equilibrium and growth forms.\(^1\),\(^4\)

Let \(\lambda(z, z - 1)\) be the distance between layers \(z\) and \(z - 1\). It is evident that in the case of crystals with complex crystallographic symmetry, which is the case for garnets, the elementary crystallographic cell consists of several layers, and therefore its characteristic size is more than one distance between layers \(\lambda\). Therefore the crystal growth rate is defined as

\[
R = \sum_{z_p, v} \frac{1}{n(z)} \cdot \frac{d C^\theta_p(z)}{d t} \langle \lambda(z, z - 1) \rangle.
\]  

(2.7)

Here \(\langle \lambda(z, z - 1) \rangle\) is the average distance in an elementary crystallographic cell between layers. Also \(n(z)\) is the number of sublattices, the sites of which belong to the layer \(z\), and the summation is taken over all its sublattices, \(n(z) \leq k\).

2.4 Free Energy of a System

In this section we will consider the problem how we can derive from the kinetic equations in the space of concentrations \(\{C^\theta_p(z)\}\) of different kind of cells, a functional \(F\) playing the role of free energy.

Equilibrium conditions between a crystal and liquid phase are determined by the stationary solutions of kinetic Eq. (2.6) \(d C^\theta_p(z)/dt = 0\). On the other hand, they result especially from the conditions for the occurrence of an extreme value:

\[
\frac{\partial F}{\partial C^\theta_p(z)} = 0.
\]

The operator \(\psi\) with components

\[
\psi^\theta([C^\theta_p(z)]) = \frac{\partial F}{\partial C^\theta_p(z)}
\]

is a potential operator in the space of concentrations \(\{C^\theta_p(z)\}\). Thus the problem arises to reduce Eq. (2.6) to potential form when the right part of Eq. (2.6) or the right part of an independent combination of Eq. (2.6) is presented.
in the form of a potential operator $\hat{\psi}$. It means the following.

Let the operators $\hat{\chi}(\{x_\gamma\})$, determined in the space of variables $\{x_\gamma\}$, be the right parts of Eq. (2.6):

$$\frac{dx_i}{dt} = \chi_i(\{x_\gamma\}),$$  \hspace{1cm} (2.9)

where $x_\gamma$ denote the required concentrations $C^q_i(z)$.

From the theorems of functional analysis it follows, that as a necessary and sufficient condition for the operator $\hat{\chi}$ potentiality the following conditions of the Jacobian matrix symmetry have to be satisfied:

$$\frac{\partial \chi_i}{\partial x_j} = \frac{\partial \chi_j}{\partial x_i}.$$  \hspace{1cm} (2.10)

This requirement is evidently in accordance with the determination of the potential operator (2.8). In the case when $\hat{\chi}$ in Eq. (2.9), i.e. in Eq. (2.6)—does not present the potential operator, there arises the necessity to use another system of equations

$$\frac{dy_i}{dt} = \psi_i(\{y_\gamma\}),$$  \hspace{1cm} (2.11)

where $y_\gamma$-independent combination of $\{x_\gamma\}$, so that in equilibirum

$$\frac{dx_i}{dt} = \frac{dy_j}{dt} = 0$$

and $\hat{\psi}$ is the potential operator. So again from the theorems of functional analysis it follows,\(^{15}\) that the functional $F(\{y_\gamma\})$ is constructed by the potential operator $\hat{\psi}(\{y_\gamma\})$ as follows:

$$F(\{y_\gamma\}) = \sum_{\gamma,i,p,\nu} N^p_i(z) \int_0^\lambda (y_i - a_i)p_\gamma(y_j + t(y_j - a_j))dt$$  \hspace{1cm} (2.12)

where the values $a_i$ determine in $\{y_\gamma\}$-space the coordinates of a point in some neighbourhood of which the functional $F$ exists. It is proved\(^{15}\) that from Eq. (2.12) the functional is defined accurately up to an arbitrary constant.

Making use of (2.8), (2.10), (2.11), (2.12) for a set of kinetic equations (2.6) we obtain the following expression for the free energy:
\[ F = \sum_{z,q,v,p} kTN^0(z) \left\{ \left[ \frac{\Delta \mu_v}{kT} + (m_{pq}^{\nu q}(z - 1, z) \\
+ m_{pq}^{\nu q}(z - 2, z) + r_{pq}^{\nu q} \right) \frac{\phi_{pq}}{kT} - \theta_v \right] C^p(z) \\
+ n_{pq}^{\nu q}(z)C^q(z)C^p(z) \frac{\phi_{pq}}{2kT} + m_{pq}^{\nu q}(z - 1, z)C^p(z) \\
\cdot \ln[C^q(z - 1) - C^q(z)] - m_{pq}^{\nu q}(z + 1, z)C^p(z) \\
\cdot \ln[C^p(z) - C^q(z + 1)] + [m_{pq}^{\nu q}(z + 1, z) - 1]C^p(z)\ln C^p(z) \\
+ [m_{pq}^{\nu q}(z - 1, z) - 1][1 - C^q(z)]\ln[1 - C^q(z)] \right\} \]  

(2.13)

Here \( F \) is counted from its value in the liquid phase, so that at \( C^p = 0 \) for all \( z \) the value of \( F = 0 \). The cells of the \((q, \gamma)\) sublattice are the nearest neighbours to the \((p, \nu)\) sublattice cells. Also the value \( N^0(z) \) denotes the number of \((p, \nu)\)-sublattice cells in layer \( z \). The free energy change, when the interface as a whole is shifted by \( z_0 \) interlayer distances corresponding to the elementary crystallographic cell size, may be given by the following expression:

\[ \Delta F = \sum_{z \leq z \leq z + z_0} N^0(z) \left\{ \Delta \mu_v + \left( m_{pq}^{\nu q}(z - 1, z) \\
+ m_{pq}^{\nu q}(z - 2, z) + \frac{n_{pq}^{\nu q}(z)}{2} + r_{pq}^{\nu q} \right) \phi_{pq} - kT \theta_v \right\} \]  

(2.14)

As a consequence we find for the chemical potential difference of liquid and solid phases:

\[ \Delta \mu_v = \partial \Delta F / \partial N_v \]

where \( N_v \) is the number of \( \nu \)-solid particles in sublattices of the elementary crystallographic cell of the crystal and we get:

\[ \Delta \mu_v = \Delta \mu_v + \sum_{q,\gamma} \left( m_{pq}^{\nu q} + \frac{n_{pq}^{\nu q}}{2} + r_{pq}^{\nu q} \right) \phi_{pq} - kT \theta_v. \]  

(2.15)

Here \( \langle \ldots \rangle \) denotes the average over the elementary cell value for corresponding coordination numbers of sublattices containing the \( \nu \)-particles. From (2.15) we derive the condition:
\[ \sum_{q,r} \left< m_{pq} \nu + \frac{n_{pq} \nu}{2} + r_{pq} \nu \right> \phi_{pq} = kT \theta_v \]  

(2.16)

with \( \theta_v \) determined according to Eqs. (2.4) and (2.5). It follows from Eq. (2.16) for a complex type of crystallographic cell, such as those of garnets that the way of dividing the crystal into layers is in general not unambiguous. However, some of these ways do not satisfy the condition (2.16), thus leading to the fact that the condition of thermodynamic phase equilibrium depends on the kinetics of processes occurring at the crystal surface. Hence these ways prove to be unacceptable for the physical system description.

2.5 Sublattice Models of \((022)_1\) faces

We can now apply the given formalism to a concrete description of the growing garnet faces \((022)_1\). The introduction of layers of connected nets when considering the step growth must satisfy the condition (2.16) and corresponds to the numbers and direction of the periodic bond chains for each crystal face.\(^1\) Figure 2.1 shows schematically how the slice can be divided into layers of connected nets for different directions of the advancing step. In order to clarify this point, interpartical distances and the crystallographic symmetry of slices at Fig. 2.1 were simplified by distorting the connected nets. Separate PBCs are indicated. However, when comparing these schematic drawings with Figs. (1.3(a) and (b)) of the first part above it is easy to identify the introduction of layers of connected nets in a real system. In addition, each lattice site of the slice (see Fig. 2.1) has a corresponding index for its sublattice \((p, v)\). Circles in Fig. 2.1a–d denote the sites having nearest neighbours in a lower slice, as shown in Fig. 1.3c–f can be seen from Fig. 2.1 that we obtain the following sublattices with the following interactions within slices and between adjacent slices.

Advance of steps by a normal to \([1/2 1/2 1/2]_1\), face \((022)_1\). Numbers

\[
k_A = k_D = k_C = 4; \]

\[
r_{1A}^C = r_{2A}^C = r_{3A}^A = r_{4A}^D = r_{2D}^A = r_{3D}^C = r_{4D}^C = r_{4D}^D = 1. \]

(2.17)

Advance of step by a normal to \([1/2 \bar{1}/2 1/2]_1\), face \((022)_1\). Numbers

\[
k_A = k_D = k_C = 4; \]

\[
r_{1A}^C = r_{2A}^C = r_{3A}^A = r_{4A}^D = r_{2D}^A = r_{3D}^C = r_{4D}^C = r_{4D}^D = 1. \]

(2.18)

Advance of step by a normal to \([0\bar{1}1]_1\), face \((022)_1\). Numbers
Fig. 2.1: Splitting of the connected net (022) into layers for the following orientations of the step edges: (a) [1/21/2]; (b) [1/001]; (c) [1/01/2]; (d) [01/1]; in case of step growth.
FIG. 2.1. (continued)
\[ k_A = k_D = k_C = 4; \]
\[ r_{1A}^D = r_{2A}^D = r_{3A}^C = r_{4A}^C = r_{1D}^A = r_{1D}^C = r_{1D}^A = r_{2D}^A \]
\[ = r_{2D}^C = r_{1C}^A = r_{1C}^D = r_{2C}^A = r_{2C}^D = 1. \] (2.19)

Advance of step by a normal to \([100]\), face \((022)_1\). Numbers

\[ k_A = k_D = k_C = 4; \]
\[ r_{1A}^C = r_{2A}^C = r_{3A}^C = r_{4A}^C = r_{1D}^C = r_{1D}^C = r_{1D}^C = r_{3D}^C \]
\[ = r_{3D}^A = r_{1C}^A = r_{1C}^D = r_{3C}^A = r_{3C}^D = 1. \] (2.20)

PART 3

3.1 Introduction

Making use of Eq. (2.9) it is not difficult to write down a set of kinetic equations for each crystallographic direction under consideration.

In the last part of this chapter (Part 3) we will consider the peculiarities of the growth kinetics and morphology of the \((022)_1\) slice based on the formalism developed above. We will then also compare the calculated and observed anisotropy of growth fronts.

It is the aim of this paper to calculate by computer the advance velocities of steps with different crystallographic directions on the \((022)_1\) slices of garnet.
and to check the role of the parameters discussed above. It will be shown that the advance velocities of the steps depend on the crystallographic directions, which results in different step profiles. At the end of this paper predicted and observed ratios of advance velocities of different crystallographic directions will be compared for the faces \{110\}.

In our calculation we suppose the following:

(i) the supersaturations for the A, D and C ions are equal or:

\[
\frac{\Delta \mu_A}{kT} = \frac{\Delta \mu_D}{kT} = \frac{\Delta \mu_C}{kT}.
\]  

(ii) the ratio of frequency factors of attachment and detachment of A, D and C ions depends only on the differences in attachment activation energies of the A, D and C ions and the temperature or

\[
\frac{\Omega_s}{\Omega_f} = \exp \left( - \frac{U_s - U_f}{kT} \right),
\]  

(iii) the role of various ratios of \(\Omega_s/\Omega_f\) of different ions in the advance velocities of steps with different crystallographic orientations is investigated.

(iv) the composition of the dissolved particles A, D and C is stoichiometric i.e.

\[
\frac{2}{3} (C_A^A)_{eq} = (C_D^D)_{eq} = (C_C^C)_{eq}
\]  

which corresponds to the formula \(D_3A_2C_3(O_{12})\) of garnet. We recall that oxygen is factored out.\(^{13-3}\) Using the fixed parameters given in (3.1) and (3.3) we will consider \(\Omega_s\) and \(\Omega_f\) as variables.

3.2 Estimation of Bond Energies

As discussed in Part 1 and Part 2 the whole theory is in essence based on a lattice gas or Ising model. This means that the whole interface garnet-mother phase is supposed to consist of equal D, A and C cells and that each of these cells can be only in two states: spin up or spin down, or in our case: solid or fluid. The bond energies occurring at the surface have then the form (where we specify for the D-bond as an example):

\[
\phi_D = \phi_D^{sf} - \frac{1}{2} (\phi_D^{ss} + \phi_D^{ff}),
\]  

where sf refers to a solid fluid bond, ss—to a solid solid bond and ff—to a fluid
fluid bond. These bonds correspond to contacts between neighbouring cells. It is difficult to calculate the real bond energies for the interface YIG–PbO flux. In the following we will describe briefly how bond energies can be estimated. We recall that we started with a system of first nearest neighbour bonds D, A and C.1)–4) Using the star tetrahedron transformation a tetrahedron with the cations D, A 2×C at the corners and oxygen in the centre is transformed into a tetrahedron without oxygen and bonds directed along the edges of tetrahedron. The problem now is to find the dimensionless energies $\phi_D/kT$, $\phi_A/kT$ and $\phi_C/kT$. Once these are known it is easy to calculate $\phi_{AD}/kT$, $\phi_{CD}/kT$, $\phi_{CA}/kT$ and $\phi_{CC}/kT$ using the formalism of Ref. (2).

In principle the ratios $\phi_D^{ss} : \phi_A^{ss} : \phi_C^{ss}$ can be obtained in two ways:

(i) Take the bond energies following from physical chemical considerations concerning the character of the bonds. This was done in Refs. (1, 3), where data of Refs. (1, 6) were chosen.

(ii) Bond energies can be calculated from a kind of Born-Haber cycle from heats of formation of crystals of ions of pure oxides. For YIG (Fe$_3$Y$_3$O$_9$) we took as a reference Fe$_2$O$_3$ and Y$_2$O$_3$.1,7) These heats of formation were in turn calculated from ionisation energies for Y$^{3+}$, Fe$^{3+}$ and O$^{2-}$, heats of evaporation from pure metals and heats of dissociation of O$_2$. The coordination of Fe in the octahedral site of garnet and hematite (Fe$_2$O$_3$) are very similar. Hence it was assumed that the energy per first neighbour bond in Fe$_2$O$_3$ and the octahedral site of YIG were the same. Similar assumptions were made for the Y$_2$O$_3$ structure. In order to calculate the bond energies of the tetrahedral sites we supposed that the total energy per cation in the AO$_6$ octahedron was the same as in the DO$_4$ tetrahedron. This makes

$$\phi_D^{ss} : \phi_A^{ss} = 3 : 2. \quad (3.5)$$

The whole calculation gives

$$\phi_D^{ss} : \phi_A^{ss} : \phi_C^{ss} = 1 : 0.67 : 0.44. \quad (3.6)$$

It is interesting to compare this with data obtained from Ref. (16) used in Refs. (4, 5) which give

$$\phi_D^{ss} : \phi_A^{ss} : \phi_C^{ss} = 1 : 0.58 : 0.37. \quad (3.7)$$

It can be seen that the ratios obtained in totally different ways do not differ much.

Since we do not know the sf and the ff bonds we introduce the so-called proportionality relation (see Eq. (3.4) and Ref. (1)):
\[ \phi_D : \phi_A : \phi_C = \phi_D^{ss} : \phi_A^{ss} : \phi_C^{ss} = 1 : 0.67 : 0.44. \] (3.8)

We note that Eqs. (3.8) and (3.7) give only the ratios and not the absolute values of bond energies. At the same time it is obvious that the ways of calculating bond energies mentioned above determine the values of bond energies \( \phi_0^{ss} \) etc. in reference to "vacuum", where the ions are infinitely far apart. Yet we need the absolute values of \( \phi_D, \phi_A \) and \( \phi_C \) in the system crystal-solution to explain the relation between bond energies and morphology and kinetics of crystal growth.

In order to solve this problem we propose the following way to make an educated guess for the absolute values of these three bond energies. We start with the experimental observations of Tolksdorf and Bartels concerning the observation of facets on a sphere of a single crystal of YIG growing from a slightly supersaturated PbO flux at about 1473 K.\(^{1,5,18,19}\) It was found, that all predicted \( F \)-faces of garnet \{211\}, \{110\}, \{321\}, \{100\}, \{210\} and \{332\}\(^{11}\) were indeed found as facets except the faces \{100\}, where due to a strong interaction (wetting) between faces \{100\} and the flux, these crystal faces grow as rough faces.\(^{1,3,5}\)

It is now interesting to note that since even the weakest faces \{332\} corresponding to the connected net \{332\} in the crystal as a very small facet (see also Refs. (5, 19)), it is therefore reasonable to assume that for this face the actual dimensionless temperature \( \theta \) and the dimensionless Ising temperature \( \theta^C \), (which corresponds to the roughening transition), do not differ much. (For a discussion of the concept of \( \theta \) and \( \theta^C \) we refer to Ref. (4) and for garnet Refs. (1, 3, 4, 5)). This is supported by the observation that this surface corresponds to a small facet and that this facet disappears at rather low supersaturations.\(^{20}\) So we can assume that

\[
\theta_{(322)_h} \leq \theta^C_{(322)_h}. \] (3.9)

It follows from the formalism of Refs. (3) and (4) that by definition

\[
\left( \frac{\phi_D}{kT} \right)^C = \frac{2}{\theta^C}. \] (3.10)

Here \((\phi_D/kT)^C\) corresponds to the bond energy divided by \(kT\) of the Ising temperature. We have carried out calculations for the Ising temperatures of the six dominant connected nets of garnet for YIG, using both the ratio of bond energies according to Eqs. (3.5) and (3.6) and we found for Eq. (3.6)

\[
\left( \frac{\phi_D}{kT} \right)_{(332)_h}^C = 4.2, \] (3.11)
and for Eq. (3.7)

\[
\left( \frac{\phi_D}{kT} \right)_{(332)}^C = 4.8. \tag{3.12}
\]

In Table 1 we have presented two sets of values of \( \phi_D/kT \) and the resulting \( \phi_{AD}/kT, \phi_{AC}/kT, \phi_{CD}/kT \) and \( \phi_{CC}/kT \) values calculated from the star-tetrahedron transformation given in Ref. (2). We used here the ratio of Eq. (3.6). It follows from Eq. (3.11) that the dimensionless energies \( \phi_D/kT \) and the resulting \( \phi_{AD}/kT \) etc. values for the sphere experiments of Tolksdorf and Bartels\(^{18}\) carried out at about 1473 K are equal or somewhat higher than the values corresponding to the highest temperatures of Table 1. We have added in Table 1 another set of dimensionless energy values to check the influence of higher bond energies or lower temperatures in the following.

### TABLE 1.

<table>
<thead>
<tr>
<th></th>
<th>( \phi_D/kT )</th>
<th>( \phi_{AD}/kT )</th>
<th>( \phi_{CD}/kT )</th>
<th>( \phi_{AC}/kT )</th>
<th>( \phi_{CC}/kT )</th>
</tr>
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<td>4.17</td>
<td>2.09</td>
<td>1.23</td>
<td>0.58</td>
<td>0.49</td>
<td></td>
</tr>
<tr>
<td>7.97</td>
<td>4.00</td>
<td>2.35</td>
<td>1.108</td>
<td>0.936</td>
<td></td>
</tr>
</tbody>
</table>

#### 3.3 Choice of Ratio of Frequency Factors (9)

We will vary the ratios \( \Omega_A/\Omega_C \) and \( \Omega_D/\Omega_C \) in our calculations in the following way (see Eq. (2.1) above):

\[
5 \cdot 10^{-3} \leq \frac{\Omega_A}{\Omega_C} = \frac{\Omega_D}{\Omega_C} \leq 1. \tag{3.13}
\]

This means that the activation energy for the entrance of \( \text{Fe}^{3+} \) ions of YIG into the tetrahedral and octahedral sites is equal or higher than the activation for the entrance of \( \text{Y}^{3+} \) ions in the dodecahedral sites. We may assume that the interaction of the oxygen ions with the \( \text{Y}^{3+} \) ions in the PbO flux is weaker than the interaction of the \( \text{Fe}^{3+} \) ions in the PbO flux, because the weaker the bonds in the crystalline phase the weaker also the bonds in the flux. This is consistent with the proportionality relations as given by Eqs. (3.6) and (3.7) above. We have to bring into consideration, however, that the coordination in the crystalline phase and the flux is for \( \text{Y}^{3+} \) two to 1.5 times higher than for \( \text{Fe}^{3+} \). In
this connection it is interesting to mention the papers of Gönnert\textsuperscript{21}) and Fischer\textsuperscript{22}) and Fischer \textit{et al.}, \textsuperscript{23,24}) where it is reported that it is found from cryoscopie experiments that the coordination of Y\textsuperscript{3+} in the PbO flux is 1.5 times larger than for Fe\textsuperscript{3+}. Taking into account Eq. (3.6) it is found that the ratio of the average energy of Fe\textsuperscript{3+} ($E_{Fe^+}$) over the energy of Y\textsuperscript{3+} ($E_{Y^+}$) in the flux is given by

$$E_{Fe^+} : E_{Y^+} = 1 : 0.80.$$  \hspace{1cm} (3.14)

It is now reasonable to assume that the higher these energies the higher the corresponding activation free energies and the lower the probability to enter the crystal lattice. This justifies Eq. (3.13). The presupposition that the Y\textsuperscript{3+} ions are more loosely bound in the PbO flux than the Fe\textsuperscript{3+} ions seems to be agreement with recent findings of Fischer, Linzen and Sinn resulting from electrochemical experiments.\textsuperscript{25})

3.4 Results of Computer Calculations

In Figs. 3.1(a) and (b) the advance velocities of steps with orientations (1)-[011], (2)-[1/2 1/2 1/2], (3)-[100] and (4)-[1/2 1/2 1/2] of the connected net (022)\textsubscript{1} are given (see also Figs. 1.3(a) and (b) of Part 1 and Figs. 1.2(a)–(d) of Part 2). Here the values $\phi_{AD}/kT=2.09$ etc. of Table 1 are used. For Fig. 3.2(a) we take $\Omega_A/\Omega_C=\Omega_D/\Omega_C=1$ and for Fig. 3.2(b) the values $\Omega_A/\Omega_C=\Omega_D/\Omega_C=5\cdot10^{-3}$, i.e. the extremes of Eq. (3.13).

We note from Fig. 3.1 that at low supersaturations for values $0\leq\Delta\mu\leq\Delta\mu^*$ the advance velocity for the step [010] is zero. This is in conflict with Monte Carlo simulations of the advance velocities of steps and must be attributed to the fact that in our sublattice model not the whole spectrum of fluctuations of the interface atomic profile is taken into consideration. Thus in the range of $0\leq\Delta\mu\leq\Delta\mu^*$ at $\Delta\mu^*>0$ the results of calculations in terms of kinetic equations should be defined based on the distribution function approximation of the orders higher than those used here.

In Figs. 3.1(c) and (d) a polar plot of these advance velocities is presented. In Fig. 3.2(a) the same advance velocities of the same steps as in Figs. 3.1(a) and (b) are given. Now the bond energies $\phi_{AD}$ etc. are higher, namely $\phi_{AD}=4.00$ etc. (see Table 1) and $\Omega_A/\Omega_C$ etc. are the same as in Fig. 3.1(b). They may be interpreted either as higher values of bond energies, or as lower temperatures in comparison with that for the results in Figs. 3.1(a)–(d). In Fig. 3.2(b) the corresponding polar plot is given.

3.5 Comparison of Theory with Experiments

From Figs. 3.1(a)–(d) and 3.2(a) and (b) a derivation of the two
Fig. 3.1. (a) Advance velocity of steps $R$ in dependence on supersaturation $\Delta \mu / k T$ for the connected net (022). The activation energies correspond to $\Omega_A/\Omega_c=\Omega_B/\Omega_c=1$. Curve (1) denotes a step with an edge direction [011]; curve (2)―a step [1/2 1/2 1/2]; curve (3)―a step [100]; curve (4)―a step [1/2 1/2 1/2]; curve (5)―a double step. Dimensionless bond energies used for calculation are given by the highest temperatures of Table 1 ($\phi_0/k T=4.17$ etc.). (b) The same dependence as in (a). Here $\Omega_A/\Omega_c=\Omega_B/\Omega_c=5 \cdot 10^{-3}$. Dimensionless bond energies used for the calculation are given by the highest temperature of Table 1 ($\phi_0/k T=4.17$ etc.). (c) Relative step advance velocities for the connected net (022). Direction and length of arrows correspond to the direction and dimensionless values of the step advance velocities. Symbols at the arrows denote the step edge orientations. Activation energies of the growth units correspond to $\Omega_A/\Omega_c=\Omega_B/\Omega_c=1$. Dimensionless bond energies correspond to the higher temperature values of Table 1 ($\phi_0/k T=4.17$ etc.). (d) The same as in (c). Here $\Omega_A/\Omega_c=\Omega_B/\Omega_c=5 \cdot 10^{-3}$. Dimensionless bond energies correspond to the higher temperature values of Table 1 ($\phi_0/k T=4.17$ etc.).
dimensional growth forms bounded by steps resulting from spiral growth or repeated two dimensional nucleation becomes possible. It follows from the network analysis of the garnet structure based on the Hartman Perdok theory that in the [1/2 1/2 1/2] and [1/2 1/2 1/2] directions two different steps occur in two adjacent connected nets (022). Due to the difference in step structure of the two steps we may suppose that the advance velocities of the steps are different and that interlacing step patterns will develop as described in Ref. (1).

This is caused by the following crystallographic peculiarities of a layer growth of (022)$_1$-slice. We choose a certain (022)$_1$ slice. The next slice, placed above it, has a mirror orientation in reference to the first slice due to a glide plane perpendicular to the slices. Therefore the direction [1/2 1/2 1/2] on the chosen slice coincides with the directions [1/2 1/2 1/2] on the slice above it, in the same way the [1/2 1/2 1/2] direction on the lower slice corresponds to the [1/2 1/2 1/2] on the slice above it (see Figs 1.3(a) and (b) in Part 1). As follows from Figs. 3.1(a)–(d) the advance rates of steps [1/2 1/2 1/2] and [1/2 1/2 1/2] are different. This difference will cause the formation of double steps since a faster growing step will overtake a slower growing step. The advance direction
Fig. 3.2. (a) The same dependence as in Fig. 3.1(a). Here $\Omega_{\lambda}/\Omega_c = \Omega_{\beta}/\Omega_c = 5 \cdot 10^{-3}$. Dimensionless bond energies used for the calculation are given by the lowest temperatures of Table 1 ($\phi_0/kT = 7.97$ etc.). (b) The same as in Fig. 3.1(c). Here $\Omega_{\lambda}/\Omega_c = \Omega_{\beta}/\Omega_c = 5 \cdot 10^{-3}$. Dimensionless bond energies correspond to the lowest temperature values of Table 1 ($\phi_0/kT = 7.97$ etc.).

of such steps coincides with the directions perpendicular to $[1/2 1/2 1/2], [1/2 1/2 1/2]$, along which the growth rate is minimal. Figures 3.1(a)–(d) show that it is the direction perpendicular to $[1/2 1/2 1/2]$. Now we assign as a reference system the crystallographic direction in a certain chosen (022); slice. Then, if the edge of the double step in the lower layer, oriented along $[1/2 1/2 1/2]$ occurs on the chosen face slice, the edge of the double step in the lower,
oriented along \([1/2 1/2 1/2]\) occurs on the upper slice, above the fixed face slice (for an upper slice this is the \([1/2 \bar{1}/2 1/2]\) direction) and so on. Therefore, both using the argument of Ref. (1) and the results of our computer calculation we can explain interlaced step patterns including the double step formation observed in the experiment to be discussed now.

It was shown in Ref. (1) that step patterns can be predicted on a \((022)_1\) slice having double step heights in the \([1/2 1/2 1/2]\) and \([1/2 \bar{1}/2 1/2]\) directions and single step heights in the \([100]\) and \([0\bar{1}1]\) directions. This is because in the last two directions the phenomenon that two steps on top of each other having different crystallographic structures and hence different advance velocities does not occur.

In Figs. 3.1(a)–(d) and 3.2(a), (b) the results of computer calculations of a fast moving step on top of a slow moving step are presented (see curve 5). It can be seen that the double height step has an advance velocity in between the slowest moving and the fastest moving step.

In Figs. 3.3 a complex spiral-like figure is presented, observed on the \((011)\) face of YIG growing from a PbO flux. This spiral was observed with phase contrast microscopy at relatively low temperatures of about 1173 K by one of us. (K.T.). The heights of the steps are about 8 nm corresponding to 7 or 8 monomolecular stepheights. The step pattern is complex mainly because of the splitting of thick steps into thinner steps. This phenomenon is pronounced especially in the \([0\bar{1}1]\) and \([100]\) directions, which can more clearly be seen when the growth temperature is increased, to 1273 K.

Fig. 3.3. Complex spiral pattern of the \((011)\) face of YIG growing from a PbO flux at relatively low temperatures of about 1173 K. The direction \([110]\) and \([001]\) are clearly different from other directions. A kind of interlacing can be observed.
As shown in Ref. (26), the step height becomes less and the spiral steps become more isotropic on increasing the growth temperature. In Fig. 3.4 a part of a real monomolecular interlaced step pattern is seen on a (011) face of YIG growing from a PbO flux at a temperatures of about 1273 K. The height of steps oriented in the [1/2 1/2 1/2] and [1/2 \( \overline{1} \) 2 1/2] directions have a double height of 9 nm, which split into sets of thinner steps with 4.5 nm height in the directions [01\( \overline{1} \)] and [100]. As the temperature is increased to about 1373 K, no interlaced steps developed due to the disappearance of anisotropy.\(^{26}\)

Upon the comparison of Figs. 3.1(a)–(d) and 3.2(a), (b) it can be seen that the higher \( \phi_{AD}/kT \) etc. the higher the differences between the advance velocities of steps, the higher the anisotropy, and from this we may conclude that the more pronounced the phenomenon of interlacing will be. From the results presented in Figs. 3.1 and 3.2 it follows that at the given value of \( \Omega_A/\Omega_C \) with an increase of temperature the two dimensional growth forms become more rounded and the anisotropy of the two dimensional growth forms becomes less.

This result of the theory is in agreement with observations. Double and higher steps are especially formed at lower temperatures 1173 \( \sim \) 1273 K (see Figs. 3.3 and 3.4), though interlaced spiral step patterns were also observed by Hergt and Pfeiffer for YIG growing from other PbO flux at about 1373.\(^{25}\) Very beautiful interlaced spirals with 10 to 50 layers thick were observed by Zamozkij and Klevsov on YIG crystals growing under hydrothermal conditions\(^{28}\) as well. It cannot be explained why with such high steps these very regular interlaced spirals develop. One would expect a more irregular pattern as given in Fig. 3.3. The relatively very low temperatures may be partly

![Fig. 3.4. Interlaced step pattern for double steps and single steps in the [100] direction. The (011) face of YIG grown from a PbO flux at about 1273 K.](image-url)
Simulation of the Advance Velocities

responsible for this. In this connection it is interesting to note that if the
temperatures become higher than say 1373 K no interlaced spirals are
observed.\textsuperscript{26}

The results of the calculations given in Figs. 3.1(a)–(d) allow us to draw
interesting conclusions on how the difference in activation energies of the
attachment to the crystal of growth units influences the growth kinetics. It
follows from our calculations that the ratio of the advance velocity of the [0\ 11]
step over the advance velocity of the [100] step increases if the ratios \( \Omega_A/\Omega_C \)
decrease. Looking at the ratio of advance velocities (subscripts at the advance
velocities denote the step edge orientations) it can be seen from Fig. 3.1 that

at \( \phi_D/k T=4.17 \) etc. and \( \Omega_A/\Omega_C=\Omega_D/\Omega_C=1 \),
\[
R_{[0\ 11]} : R_{[100]} : R_{[1/2\ 1/2\ 1/2]}^{\text{fast}} : R_{[1/2\ 1/2\ 1/2]}^{\text{slow}} : R_{[1/2\ 1/2\ 1/2]}^{\text{double}} = p : q : r : s : u = 1 : 0.63 : 0.73 : 0.20 : 0.20
\]
\[
(3.15)
\]
at \( \phi_D/k T=4.17 \) etc. and \( \Omega_A/\Omega_C:\Omega_D/\Omega_C=5 \cdot 10^{-3} \),
\[
p : q : r : s : u = 1 : 1.08 : 1.21 : 0.81 : 0.89,
\]
\[
(3.16)
\]
and at \( \phi_D/k T=7.97 \) etc. and \( \Omega_A/\Omega_C:\Omega_D/\Omega_C=5 \cdot 10^{-3} \),
\[
p : q : r : s : u = 1 : 1.25 : 0.94 : 0.24 : 0.80.
\]
\[
(3.17)
\]

From experimental data at 1173 K (Fig. 3.3) and 1273 K (Fig. 3.4)\textsuperscript{26,9}
we receive
\[
p : q : u = 1 : 1.15 : 1.01
\]
\[
(3.18)
\]
\[
p : q : u = 1 : 1.09 : 0.90,
\]
\[
(3.19)
\]
respectively. So upon comparing the experimental anisotropy in advance
velocities of monomolecular steps at 1273 K and adjusted calculated
parameters which match the observed ratios in advance velocities, we
conclude that
\[
\Omega_A/\Omega_C = \Omega_D/\Omega_C = 5 \cdot 10^{-3}
\]
\[
(3.20)
\]
and the set of bond energies corresponding to the highest temperatures of
Table 1 give the best results. It is interesting to note that we have already
predicted in Section 3.2 that the activation energies for Fe\textsuperscript{3+} ions are expected
to be higher than for Y\textsuperscript{3+} ions.

### 3.6 Waiting Times

Let us now consider certain fundamental peculiarities of the kinetic
model used here. Figure 3.5 presents the dependence of the step width on supersaturation $\Delta \mu / k T$. For all the analysed directions there exists a kinetic transition from an atomically-smooth interface to a rough one. It is evident from Fig. 3.5 that this transition may be characterized by the supersaturation interval $\Delta \mu_R / k T$ at which it takes place. We should note that this roughening transition is independent of the critical supersaturation which exists in a model.

Figure 3.2 shows the calculated results of the step advance velocity at a face (022)$_1$. As follows from Fig. 3.2, in this case the critical supersaturation is $\Delta \mu^* = 0$ and the kinetic roughening transition occurs independent of the value of $\Delta \mu^*$. We note that the values of $\Delta \mu_R$ are high ($1.5 < \Delta \mu_R / k T < 2.5$) and this effect is of purely theoretical interest.

In the region of the supersaturations $\Delta \mu$-lower than $\Delta \mu_R$ the roughness of the atomic profile of the step edge is low, so that the step width does not exceed five layers. This determines the existence of a sublattice, in which the growth units of different kinds fill the cells in different sublattices and this sequence depends on the parameters of interaction $\phi_T / k T$, of the crystallographic step orientation and supersaturation $\Delta \mu / k T$. Figure 3.6 illustrates these data for a step, which edge is oriented along direction [011] ($\Delta \mu / k T = \ln 3$). It follows
from our calculations for the growth of a multicomponent crystal with a complex lattice symmetry, that in order to describe the kinetics we should also take into account certain characteristic parameters—such as waiting times $\tau_{\gamma}^q$. Here the parameter $\tau_{\gamma}^q$ of a particle $(q, \gamma)$ denotes the interval of the time between the moment when the particle $(q, \gamma)$ attaches to the step edge and the attachment of a previous growth unit. Figure 3.8 presents the estimated values of $\tau_{\gamma}^q$ for different $\Delta \mu$ for the step [011] advancing on a slice (022). It is clear that at $\Delta \mu \rightarrow 0$ the values of $\tau_{\gamma}^q$ increase. From Fig. 3.7 it follows that $\tau_{\gamma}^q \rightarrow 0$ if $\Delta \mu > \Delta \mu_R$, which is above the kinetic roughening transition point. Even in the absence of a critical supersaturation, large values of $\tau_{\gamma}^q$ at $\Delta \mu < \Delta \mu_R$ determine the fluctuations both of the rate $R_{\gamma}^q$ when $(q, \gamma)$-particles attach to the step edge, and its advance velocity $R$ (see Fig. 3.8). Thus the waiting time $\tau_{\gamma}^q$ is defined by a distance between the maximum rate $R_{\gamma}^q$ and the nearest to it proceeding rate maximum $R_{\gamma}^p$ of another particle’s attachment (for example, in Fig. 3.8 these are $-R_{\gamma}^A$ and $R_{\gamma}^C$).

The existence of a waiting time different from zero is recognized by the experimental investigations on selectivity of filling up different types of cells in different sublattices by different types of doping impurity.$^{20}$

In Ref. (21) the growth kinetics was considered of (111)-faces of garnets Y$_3$Fe$_5$O$_{12}$, based on the introduction as growth units of an elementary crystallographic cell containing many A, D, C-ions. This approach evidently holds true if the waiting times $\tau_{\gamma}^q$ are small, that is at $\Delta \mu > \Delta \mu_R$. 

**Fig. 3.6.** The sequence in which the growth units attach to the edge of the steps advancing in the direction perpendicular to [011] (it is indicated by Roman figures). Face (022). Here $\Omega_\lambda/\Omega_\infty=\Omega_0/\Omega_\infty=0.02$; $\exp(\Delta \mu/kT)=3$. Nondimensional bond energies correspond to the higher temperatures in Table 1.
Fig. 3.7. The waiting time $\tau$ dependence on supersaturation $\Delta \mu / k T$. Face (022). Curve (1) shows the waiting time of a particle IX (see Fig. 3.6) for a particle I, curve (2)—of a particle XI for a particle VI, curve (3)—of a particle XII for a particle II.

Fig. 3.8. Complete step advance velocity $R$ and the component part $R_0^c$ of advance velocity in sublattices ($q, \gamma$) as a function of nondimensional time $t$. Slice (022)$_t$. Advance of a step [011], $\exp(\Delta \mu / k T)=3$; $\Omega_A/\Omega_C=\Omega_D/\Omega_C=0.02$. In Fig. 3.6 sublattice (1, A) is denoted by a Roman figure IX, sublattice (1, D)—By I, sublattice (1, C)—IV. Nondimensional bond energies correspond to the higher temperatures in Table 1.
3.7 Summary and Conclusions

In this paper we have shown how starting from the crystallographic structure of the connected net (022), determined from the crystal graph of garnet, according to an extended Hartman Perdok theory (see also Ref. (5) in this book and Ref. (1)), the worlds of the crystallographic morphological theory of Hartman and Perdok and of statistical mechanical Ising models and kinetic models\textsuperscript{11-14} of the interface crystal—motherphase can be logically integrated. Such an integration not only results in a calculation of Ising temperatures of more or less complex connected nets\textsuperscript{3} but as shown in this paper also to the possibility to calculate the advance velocities of steps of different crystallographic directions in dependence of the bond energies divided by $kT$ at the surface and the relative supersaturations.

Such an integrated approach is only possible if the concepts which play an essential role in growth kinetic models based on simple Kossel like structures are generalized for complex structures.

It is shown in this paper how this can be done for the concept of kink, the solid on solid condition and the corresponding cutting of connected nets in strips. Also for each crystallographic structure the set of coupled differential equations has to be worked out.

This integrated approach is also only possible if a number of reasonable but ad hoc presuppositions are introduced. The most important is the so called proportionality hypothesis, where it is assumed that the ratio of bond energies at the surface of the bond energies $\phi_D$, $\phi_A$ and $\phi_C$ (given by (1.2)) are the same as $\phi_D^S$, $\phi_A^S$ and $\phi_C^S$ i.e. the broken bond energies in the crystal in reference to the vacuum (Eq. (3.8)).

Traditionally, apart from this condition the so called equivalent wetting condition is introduced, which makes an unambiguous calculation of the bond energies $\phi/kT$ at the surface possible. This second condition implies that it is assumed that the motherphase is homogeneous up to the solid surface, so making the bonds between a solute growth unit and the motherphase the same as the corresponding bonds at the surface. It has been explicitly shown for the case of YIG growing from a PbO flux that this second condition has to be abandoned (see Ref. (5) and Ref. (19)). In order to estimate the bond energies we then started with the sphere experiments of Tolksdorf and Bartels.\textsuperscript{18} From the fact that the weakest (332) face still did occur as a flat face and that it was supposed to be close to the roughening temperature, we made an estimate of the actual $\phi_D/kT$, $\phi_A/kT$ and $\phi_C/kT$ values at the surface. Using the proportionality relation we then did arrive at ratios of advance velocities of steps of four different crystallographic directions in good agreement of advance velocities of monomolecular steps observed with refined phase contrast techniques. We had to assume, however, that the frequencies of attachment of the $Y^{3+}$ ions were five hundred times larger than of the $Fe^{3+}$ ions.
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