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## Modeling and Numerical Simulation of Diffusion Induced Segregation

Two mathematical models for describing diffusion induced segregation (DIS) in the case of a (Zn,Fe)S single crystal are derived and discussed. The second is formulated within the Ginzburg-Landau theory and implies special concentration dependent free energies. Numerical simulations in 2-d capture significantly the properties of natural chalcopyrite DIS phenomena and allow for the first time quantitative descriptions. The calculations predict convex free electron distributions within the single crystal that are beyond the resolution of today's measuring instruments.

Keywords: structure gradients, Ginzburg-Landau theory, reaction-diffusion equations

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### 1. Introduction

High amounts of solid state exsolutions are often observed in nature but cannot only be explained by systems exceeding maximal concentrations of e.g. temperature depending solid solution series. Especially the so-called chalcopyrite disease within sphalerite (figure 1) can only be obtained from primary mineral assemblages by irreversible diffusion induced segregation (DIS). The corresponding thermodynamical conditions were firstly determined by BENTE & DOERING (1993, 1995) by experimental simulations. The chalcopyrite DIS within sphalerite is caused by gradients of the chemical potential induced by an increase of external sulphur fugacity and by copper diffusing into a Fe-containing sphalerite crystal. Hereby, the primary  $\text{Fe}^{2+}$  is oxidized to  $\text{Fe}^{3+}$  and reacts with the copper to  $\text{CuFeS}_2$ . In section 2 we give a concise picture of the observed reaction by splitting it into several steps.

Yet, this thermodynamic and kinetic knowledge based on the experimental DIS-simulations does not explain quantitatively nor predict all DIS phenomena, mathematical simulations have to be done. In this article, a system of partial differential equations is derived and corresponding numerical calculations are carried out. The introduced model supplies a possible mechanism for the segregation process that results in a better common understanding of all solid state segregation reactions in materials. The numerical calculation gives for the first time quantitative data of the DIS.

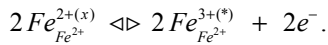
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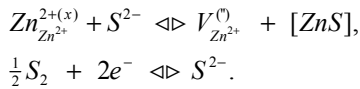
## 2. The single steps of the chalcopyrite disease

Within the thermodynamic and kinetic experiment simulation the chalcopyrite DIS primary (Zn,Fe)S single crystals receptors are embedded in Cu-Fe-S-powders (300°C-700°C) working as Cu sources. Solid state buffers (Fe/FeS, Fe<sub>1-x</sub>S/S, Fe<sub>1-x</sub>S/FeS<sub>2</sub>, Cu<sub>2</sub>S/CuS) realize the external sulphur fugacity. At temperature greater than 550°C chalcopyrite (CuFeS<sub>2</sub>) is transformed to cubic ISS (intermediate solid solution). The following partial processes and their local implications have to be algorithmized for the mathematical simulations:

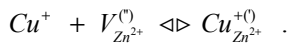
1. Oxidation of Fe in (Zn,Fe)S and release of electrons in the crystal:



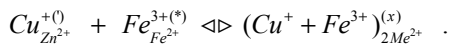
2. S<sup>2-</sup>-reduction at the Zn-S-gas interface, diffusion of Zn out of the sphalerite crystal, vacancy formation ( $V^*$ ) in ZnS and attachment of Zn<sup>2+</sup> + S<sup>2-</sup> forming [ZnS] at the sphalerite rim:



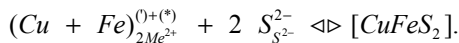
3. Cu-diffusion and vacancy occupation by Cu:



4. Cu-Fe-Clustering due to the electrostatical attraction of Cu and Fe:



5. Nucleation and segregation of CuFeS<sub>2</sub>:



The notations are:

$Cu_{Zn^{2+}}^{(*)}$  : Cu<sup>+</sup> occupying a Zn<sup>2+</sup> position, hence negatively charged (\*).

$Fe_{Fe^{2+}}^{3+(*)}$  : Fe<sup>3+</sup> occupying a Fe<sup>2+</sup> position, hence positively charged (\*).

$V_{Fe^{2+}}^*$  : vacant Fe<sup>2+</sup> position, hence double negatively charged (\*\*).

[ZnS]: electrically neutral phase.

Based on additional experimental work and Moessbauer studies, the maximal Fe<sup>3+</sup> related the overall Fe-content of (Zn,Fe)S cannot exceed 7% at naturally occurring sulphur fugacities given by a Fe<sub>1-x</sub>S/FeS<sub>2</sub> buffer.

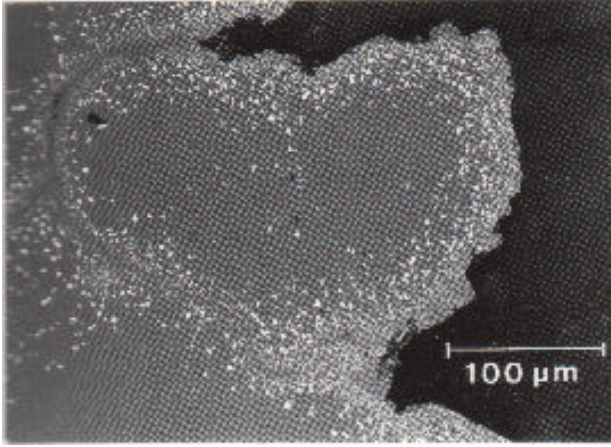


Fig. 1: Reflected light image of a polish section of natural chalcopyrite disease within sphalerite disease from Nigeria (dark matrix: sphalerite, light grains: chalcopyrite)

### 3. Derivation of the general mathematical model

The starting point of the mathematical discussion are the reaction-diffusion equations in the general form, see LUCKHAUS & VISINTIN (1983),

$$\partial_t n_i = \operatorname{div}(J_i) + f_i = \left( \sum_k \frac{\partial}{\partial x_k} J_{i,k} \right) + f_i, \quad i = 1, \dots, 4. \quad (1)$$

In these equations,  $n_i = n_i(x, t)$  denotes the relative number of species  $i$ ,  $i = 1, \dots, 4$  per available lattice point at time  $t$  and space point  $x \in \Omega$ ,  $\Omega$  a domain in  $\mathbb{R}^D$ ,  $1 \leq D \leq 3$ . We introduce the notations  $n_1 \approx Fe^{3+}$ ,  $n_2 \approx Fe^{2+}$ ,  $n_3 \approx Cu^+$ ,  $n_4 \approx Zn^{2+}$ ,  $n_5 \approx$  vacancies.

$n_1$  satisfies  $n_1 = \frac{N_{Fe^{3+}}}{N_{Me}}$ , where  $N_{Fe^{3+}}$  is the number of  $Fe^{3+}$  atoms and  $N_{Me}$  is the number of metal ion sites. Similar relationships hold for  $n_2$ ,  $n_3$  and  $n_4$ . Notice that there is no equation for  $n_5$ , but the vacancy concentration is obtained implicitly by the conservation of mass:  $n_5 = 1 - \sum_{i=1}^4 n_i$ .

In (1),  $f_i$  denote the reaction terms and  $J_i$  the fluxes of metal ions of species  $i$ . The constitutive relation for the mass fluxes is assumed to be of the isotropic Onsager form

$$J_i = \sum_{j=1}^4 L_{ij} \nabla \mathbf{m}_j,$$

where  $L$ , the mobility, is a symmetric positive-semidefinite  $4 \times 4$  tensor and  $\mathbf{m}_j = \frac{\partial F}{\partial n_j}$  denotes the chemical potential.

To simplify the discussion of thermodynamics, we fundamentally assume that the temperature  $T$  is held constant. Then, let  $F$  denote the Helmholtz free energy of the system, consisting of  $F_I, F_{II}$ , with  $F_I$  for chalcopyrite,  $F_{II}$  for sphalerite. Hence, the two different phases or lattice orders are characterized by two different free energies, and  $F$  is the convex hull of  $F_I$  and  $F_{II}$ .

For order-disorder phase transitions, up to constants,  $F_I$  and  $F_{II}$  are assumed to behave like

$$F_I = \sum_{i=1}^5 \mathbf{b}_i n_i \ln n_i + \left( \sum_{i=1}^4 \mathbf{a}_i n_i \right)^2. \quad (2)$$

The second term in (2) is a consequence of Hooke's law. The constants  $\mathbf{a}_i$  measure the volume response when replacing  $Zn^{2+}$  by other metal ions and  $\mathbf{b}_i > 0$  contain the Boltzmann constant  $k_B T$  as a factor. It should be stated that the free energy (2) is reasonable because the high temperature transitions are random pairwise interactions. Furthermore, it is a very reasonable term for a numerical computation, since (2) implies infinite slope of  $DF_I$  if one component  $n_j$  approaches 0 or 1. This guarantees, see PROTTER&WEINBERGER,

$$n_j \in (0,1) \quad (3)$$

and  $n_j$  has physical meaning. As there is no maximum principle for systems of equations, without the logarithmic terms in (2), the condition (3) may be violated even if  $n_j \in (0,1)$  holds for  $t = 0$ .

$f_1 = -f_2$  is the reaction term for  $Fe^{2+} \leftrightarrow Fe^{3+} + e$ ,  $e$  a free lattice electron,  $f_3 = f_4 = 0$ . The relative number of electrons  $n_e$  is determined by the condition of electric neutrality, namely (we assume that all sulphur places are occupied by  $S^{2-}$ ):

$$n_e = 3n_1 + 2n_2 + n_3 + 2n_4 - 2.$$

The mass balance law for given reaction rate  $k$  and balance constant  $\mathbf{g}$  implies

$$f_1 = k(n_2 - \mathbf{g} n_1 n_e).$$

#### 4. Derivation of an adapted model

The above model is complete and could be used as a basis for numerical experiments. Yet, it is not well adjusted to the problem and does not exploit the special properties of chalcopyrite disease. The oxidation of Fe is caused by swift shifts of the electrons and occurs thus much faster than any other chemical process. Hence, it is reasonable to assume that this oxidation

is instantaneous. Mathematically, this means that we introduce a fast variable

$$u = n_1$$

that for fixed  $n_1 + n_2$  describes the free electrons, introduce the slow variables

$$c_2 = n_1 + n_2, \quad c_3 = n_3, \quad c_4 = n_4$$

and split the system (1) assymmetrically into one stationary elliptic equation for  $u$  and three time dependent parabolic equations for  $c_2$ ,  $c_3$  and  $c_4$ .

In the next step, due to electric neutrality, we postulate

$$n_5 = \frac{1}{2} n_1. \quad (4)$$

To be precise, relation (4) means that the movement of the vacancies is on the same fast time scale as the movement of the free electrons. This is of course an idealization of the actual situation, but relation (4) is verified by all measurements being not fast enough to notice the discrepancy.

Relation (4) allows to eliminate  $c_4$ . In fact, conservation of mass yields

$$c_4 = 1 - \frac{1}{2}c_1 - c_2 - c_3. \quad (5)$$

Finally, a control mechanism for the segregation process is introduced. Following BLESSEN, we define a phase parameter  $\mathbf{c} = \mathbf{c}(x, t) \in [0, 1]$  that measures the volume fraction of the chalcopyrite phase; e.g.  $\mathbf{c}(x_0, t_0) = 0$  means that for  $t = t_0$  in  $x_0$  only the sphalerite phase is present,  $\mathbf{c}(x_0, t_0) = \frac{1}{2}$  that the system is in  $x_0$  in an intermediate state with no dominant phase.

We introduce the entropy of mixing  $S_M$  of the system as

$$S_M(\mathbf{c}) = W(\mathbf{c}) + \frac{1}{2}(\mathbf{e} \cdot \nabla \mathbf{c})^2, \quad W(\mathbf{c}) := \mathbf{c} \ln \mathbf{c} + (1 - \mathbf{c}) \ln(1 - \mathbf{c}) - \frac{1}{2} \mathbf{c}^2. \quad (6)$$

The thermodynamic relation  $F = E - TS$  implies that the free energy  $F$  is the sum of  $S_M$  and the convex combination of  $F_I$  and  $F_{II}$ :

$$F(u, c_2, c_3, \mathbf{c}) := \mathbf{c} F_I(u, c_2, c_3) + (1 - \mathbf{c}) F_{II}(u, c_2, c_3) + T S_M(\mathbf{c}).$$

With these settings we define

$$\mathbf{y}(c_3, \mathbf{c}) := \ln \left( \frac{\mathbf{c}}{1 - \mathbf{c}} \right) - \mathbf{c} + m(c_3). \quad (7)$$

Equation (7) will be explained in Section 6. The value  $m(c_3)$  accounts for the growing of chalcopyrite in copper rich regions.  $\mathbf{y}$  is the driving force of the modified Allen-Cahn equation governing  $\mathbf{c}$ ,

$$\partial_t \mathbf{c} = -\partial_c \left( \frac{F}{T} \right) = \mathbf{e}^2 \Delta \mathbf{c} - \mathbf{y}(c_3, \mathbf{c}), \tag{8}$$

where  $\mathbf{e} > 0$  is a small constant, denoting the thickness of the interface between sphalerite and chalcopyrite phases.

With all these modifications, we obtain the following adapted model:

Find for  $t \geq 0$  functions  $u, c_2, c_3$  and  $\mathbf{c}$ , such that in  $\Omega \subset \mathbb{R}^D$  for  $t > 0$

$$0 = \operatorname{div} \left( d \nabla \frac{\partial F}{\partial u} \right) + k(c_2 - u) - \mathbf{g} k u c_3, \tag{9}$$

$$\partial_t c_i = \operatorname{div} \left( \sum_{j=2}^3 \tilde{L}_{ij} \nabla \frac{\partial F}{\partial c_j} \right), \quad i = 2, 3, \tag{10}$$

$$\partial_t \mathbf{c} = \mathbf{e}^2 \Delta \mathbf{c} - \mathbf{y}(c_3, \mathbf{c}) \tag{11}$$

and for  $t = 0, x \in \Omega$

$$u(x, 0) = u_0(x), \tag{12}$$

$$c_i(x, 0) = c_{0i}(x), \quad i = 2, 3, \tag{13}$$

$$\mathbf{c}(x, 0) = \mathbf{c}_0(x) \tag{14}$$

and for  $t > 0, x \in \partial\Omega$

$$\partial_n u = \partial_n c_2 = \partial_n \mathbf{c} = 0, \quad c_3 = g_3. \tag{15}$$

### 5. Numerical solution method

The experience has shown that the numerical computation of reaction-diffusion equations is frequently a difficult task due to the possible occurrence of boundary layers and stability problems. A first naive idea to solving (9)-(15) is the use of a predictor-corrector method. But because of the ellipticity of equation (9), a fixed point for the iterated solutions of this scheme cannot be guaranteed and in practise the algorithm is observed to converge very slowly.

Therefore we developed a new and quite generally applicable variant of the Quasi-Newton method that in comparison to the former method allowed a speedup of a factor 100. Prior to introducing the new scheme, we first repeat Newton's method for those readers who might not be familiar with the concept.

The classical Newton iteration for finding the zero point of a differentiable function  $f$  and given start point  $x_0 \in \mathbb{R}^n$ ,

$$x_j := x_{j-1} - (Df(x_{j-1}))^{-1} f(x_j), \quad (16)$$

is a linearization of the original problem inasmuch as in practise one solves

$$A_j d_j = -f(x_{j-1}), \quad (17)$$

together with the update  $x_j := d_j + x_{j-1}$ . Iteration (17) is called a Quasi-Newton method if instead of  $A_j = Df(x_{j-1})$  an approximation of  $Df(x_{j-1})$  is used. Our implementation now consists of the setting

$$A_j z := \frac{f(x_{j-1} + \mathbf{h} z) - f(x_{j-1})}{\mathbf{h}} \quad (18)$$

for a fixed small constant  $\mathbf{h} > 0$  and to pursue the solution of the linear system (17) with the generalized minimal residual method, GMRES, see SAAD for details. For the practical implementation, only a multiplication routine  $z \mapsto A * z$  must be present and  $A$  need not be stored explicitly.

Apparently, this new variant can be easily implemented for a wide class of problems. It combines the fast convergence of Newton's method with the excellent damping properties of GMRES.

We applied the above algorithm to the weak formulation of (9)-(15) together with linear finite elements and an implicit time discretization. We skip over these technical details.

## 6. Control mechanism for the chalcopyrite phase

To understand the control mechanism for the growth of chalcopyrite phases within sphalerite, we observe that the extrema  $z$  of the Allen-Cahn equation (8) satisfy

$$\mathbf{y}(c_3, z) = 0. \quad (19)$$

Looking at equation (7), the analysis of condition (19) (e.g. with a 1-d Newton-method) reveals that for a negative value of  $m$ , the larger extremal point of  $\mathbf{y}$  is preferred whereas for positive  $m$ , the smaller extremal point has the smallest energy, see Figure 2. The mechanism was first introduced in KOBAYASHI for heat diffusion coupled with the Allen-Cahn equation to model growth of dendrites.

For the time being we only consider the simplest case where the difference of the free energies is no function of  $u$  and  $c_2$  :

$$m(u, c_2, c_3) = \partial_c \left( \frac{F}{T} \right) = \frac{F_I(u, c_2, c_3) - F_{II}(u, c_2, c_3)}{T}$$

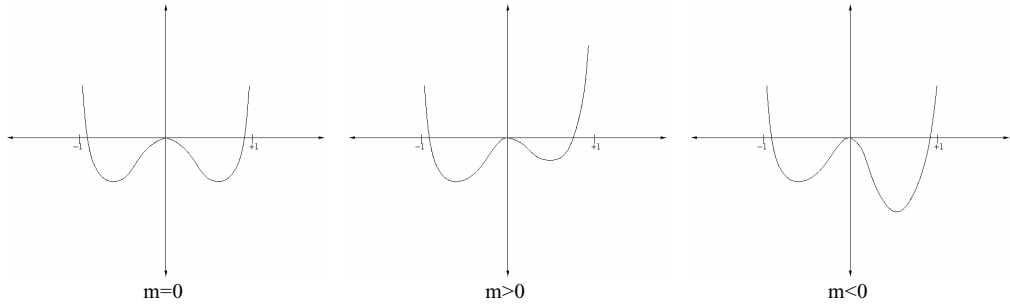


Fig. 2: Preferred phase depending on  $m$ .

In this article, we only analyse the special case  $m = m(c_3)$ . Equation (2) implies for positive constants  $\mathbf{b}, \mathbf{d}$  ( $\mathbf{b}$  depends on  $T$ )

$$m(c_3) = \mathbf{b} \ln c_3 + \mathbf{d}, \tag{20}$$

and  $\mathbf{d}$  is the difference of the additive constants of the entropy for phase I and II. Since  $m(0) = m(1) = \mathbf{d} > 0$  and  $m(1/e) = -\frac{\mathbf{b}}{e} + \mathbf{d} < 0$  for suitable  $\mathbf{b}$  and  $\mathbf{d}$ , there exist  $x_1, x_2 \in (0, 1)$ ,  $x_1 < x_2$  with  $m(x_1) = m(x_2) = 0$ , see Figure 3.

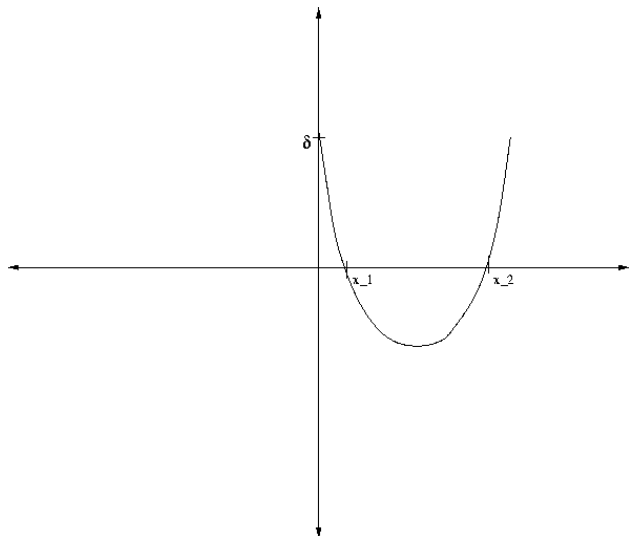


Figure 3: The graph of  $m(c_3)$ .



$x_1$  is the minimal concentration value of  $\text{Cu}^+$  to be exceeded before chalcopyrite phases can form (at  $t = 0$  the concentration of  $\text{Cu}^+$  is small in  $\Omega$ ).  $x_2$  is the maximal  $\text{Cu}^+$  concentration before the chalcopyrite phases start to destabilize. The function  $\mathbf{y}$  is defined in such a way that for small values of  $c_3$ , sphalerite is preferred whereas for  $c_3 \in (x_1, x_2)$ , the chalcopyrite phase has the lowest energy level. Physically, this means that the segregation of chalcopyrite can only take place after an sufficient amount of copper has diffused from outside into the single crystal. Instead of a polynomial approach, the extrema  $z$  of the phase parameter are no longer at 0 and 1, but are determined by condition (19). For  $\mathbf{b} = 20$  and  $\mathbf{d} = 4$  for instance one gets  $x_1 \approx 0.07$ ,  $x_2 \approx 0.77$  and we find  $z \approx 0.987$  for  $c_3 = 1/e < x_2$  and  $z \approx 0.02$  for  $c_3 = 0.001$ .

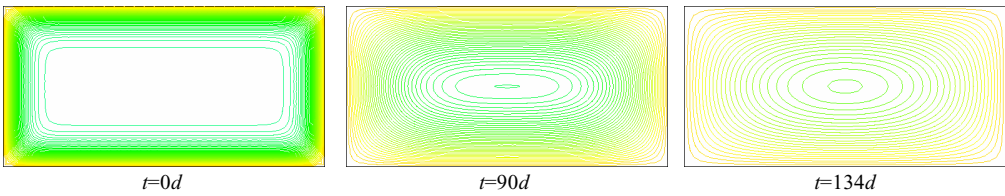


Fig. 4: Diffusion of  $\text{Cu}^+$ . The density of the level sets indicate the steepness of the copper gradient. At  $t=0d$  the initial datum falls from 0.6 at the boundary to 0.001 in the center.

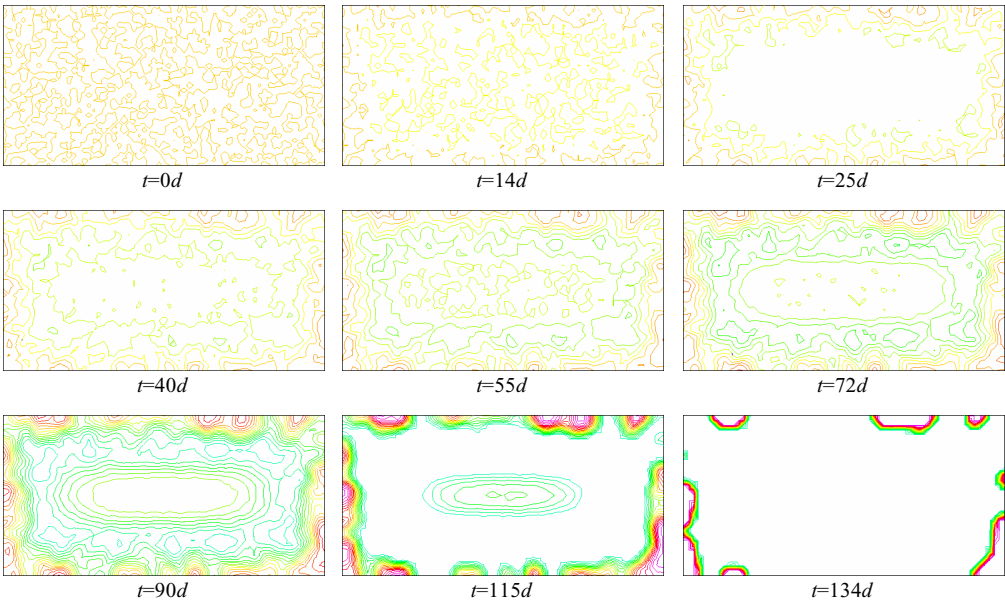


Fig. 5: Time evolution of the chalcopyrite phases. The first picture for  $t=0d$  shows the random distribution of  $\mathbf{c}$  around 0.5. Phase formation takes place until for  $t=134d$  the chalcopyrite phases concentrate near the boundary as a consequence of the copper gradient and the diffusion of copper into the crystal.

## 7. Numerical simulations

First, we present a typical simulation to illustrate the behaviour of the model. In this simulation, the underlying uniform triangulation of  $\Omega$  as well as the time step  $\Delta t$  were not adapted during the computation. The simulations were performed for a 2-dimensional layer  $\Omega$ . We solved (9)-(15) in their dimensional form and used the measured values for the physical parameters, see NELKOWSKI & BOLLMAN for the diffusivity constants.

**Physical Parameters:**  $\Omega = 1,2 \cdot 10^{-3} m \times 6 \cdot 10^{-4} m$ ,  $T = 500^\circ C$ ,  $\mathbf{g} = 0.06$ ,  $\mathbf{e}^2 = 3 \cdot 10^{-9} m$ ,  
 $D_{Cu} = 2,6 \cdot 10^{-4} m/s$ ,  $D_{Zn} = 1,85 \cdot 10^{-7} m/s$ ,  $D_{Fe} = 1,26 \cdot 10^{-4} m/s$ ,  $\mathbf{a}_1 = 1$ ,  
 $\mathbf{a}_2 = 0,9$ ,  $\mathbf{a}_3 = \mathbf{a}_4 = 0$ .

**Triangulation Data:** 6521 points, 12800 triangles,  $h = 10^{-8}$ ,

**General Parameters:**  $\mathbf{e}_{GMRES} = 4 \cdot 10^{-3}$ ,  $\Delta t = 4 \cdot 10^{-3}$ ,  $\mathbf{h} = 10^{-8}$ ,  $\mathbf{b} = 20$ ,  $\mathbf{d} = 4$ .

**Initial conditions:**  $u \equiv 0.001$ ,  $c_2 = 0.3$ ,  $c_3 = 0.001$  and  $\mathbf{c}$  a small random deviation of 0.5 in  $\Omega$ .

**Boundary conditions:**  $\partial_n u = 0$ ,  $\partial_n c_2 = 0$ ,  $c_3 = 0.6$  and  $\partial_n \mathbf{c} = 0$  on  $\partial\Omega$ .

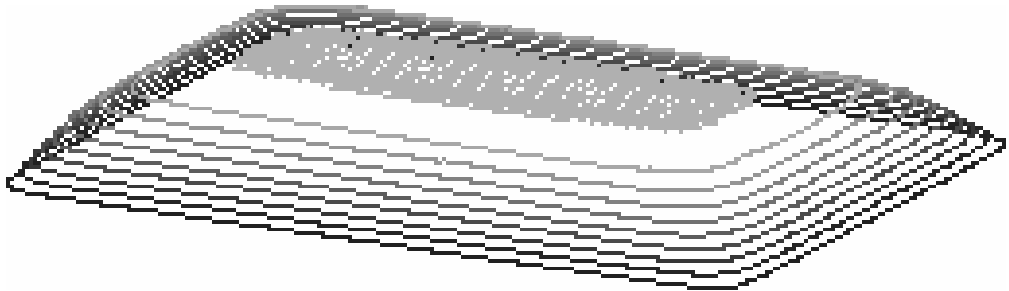


Fig. 6: Typical plot of  $Fe^{3+}$ . The graph of  $Fe^{3+}$  grows slightly to the center and is convex. The graph of  $u$  is very flat due to the predicted maximum content of  $Fe^{3+}$  on the iron concentration. The display is magnified, the maximum of  $u$  being 0.05 and the minimum 0.01.

During the computation, the graph of  $Fe^{3+}$  is flattening even more. The graph of Zn behaves opposite to the graph of  $Cu^+$ . It decreases near the boundary. The concentration of  $Fe^{3+} + Fe^{2+}$  is not displayed, it is a perfect constant in time and space. Hence, Figure 6 also tells us about the distribution of the electrons during the experiment.

## 8. Discussion of the results and outlook

As presented above, the mathematical model is capable of capturing significant features of the chalcopyrite disease. It gives new insights in the electron distribution during the experiment that cannot yet be measured experimentally. The numerical implementation supplies a quantitative description of the physical process and gives fast predictions even in situations, where the crystallographical experiments take very long (almost 6 months for cubic sphalerite at  $T=500^\circ C$ ).

Nevertheless, the model has some limitations and weaknesses:

- a) In reality, the crystal is growing during the experiments since  $S^{2-}$  ions attach to the surface. This effect is small and has been neglected in our model. For the resulting free boundary problem, it is not clear what kind of boundary conditions to impose and if long time existence of the solution still holds for  $D > 1$ .
- b) The diffusing copper dramatically perturbs the local lattice symmetry. Hence, the diffusion of copper might depend on microscale properties of the grid and the diffusivity is by no means constant as was assumed in the above calculations.
- c) The consequences of condition (3) to the system must be analysed in detail.
- d) As a consequence of (8), "mushy regions" occur.

#### *Acknowledgments*

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