Eur. Phys. J. B **13**, 395–398 (2000)

THE EUROPEAN
PHYSICAL JOURNAL B
EDP Sciences

Oscillatory zoning caused by oscillating surface relaxations

W.T. Lee[a] and E.K.H. Salje

Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge CB2 3EQ, UK

Received 9 March 1999

Abstract. Oscillatory zoning is a spatial variation in the composition of minerals. It has been observed in many different minerals and a variety of mechanisms have been proposed to explain it. We propose an equilibrium model of oscillatory zoning in which the variations in composition stabilise a ferroelastic phase. This results in a sinusoidal variation in composition. We expect that this mechanism could account for oscillatory zoning found in minerals with oscillatory surface relaxations.

PACS. 61.72.-y Defects and impurities in crystals; microstructure – 61.72.Ss Impurity concentration, distribution, and gradients – 81.10.-h Methods of crystal growth; physics of crystal growth

1 Introduction

Oscillatory crystal zoning has been observed in many minerals that have crystallised from melts and from aqueous solutions. Shore and Fowler [1] give a list of minerals in which oscillatory zoning is known to occur. It has been produced experimentally [2] in the (Ba,Sr)SO_4 system. The phenomenon consists of a variation in chemical composition that may be regular, stochastic or chaotic. Various mechanisms have been suggested to explain this phenomena. One class of explanations involves repetitive changes in the external environment of the crystallising mineral. Models based on these ideas have been put forward to explain zoning in plagioclase feldspar [3,4], and carbonates [5,6]. Another explanation uses out of equilibrium, non-linear models of crystal growth and diffusion in the boundary layer between the crystal growth front and the bulk liquid out of which the crystal is growing. Such models have been invoked to explain zoning in carbonates [7] and in plagioclase feldspar [8]. Positive and negative feedback in these models can produce oscillations. It is known that surface relaxations can affect crystal growth morphologies [9]. In this paper we propose a model in which compositional variations interact with an oscillatory surface relaxation to stabilise a ferroelastic phase transition in the crystal. We consider how to incorporate compositional variations into the (one-dimensional) free energy functional of a crystal with an oscillatory surface relaxation. We show that the existence of the extra degree of freedom associated with compositional variations may destabilise the crystal with respect to a ferroelastic transition. The new equilibrium state of the crystal has in phase sinusoidal oscillations of the strain and composition fields. This oscillatory zoned state is derived explicitly from a free energy functional that is convex for all Fourier components of the strain, but shows instability when the composition is allowed to relax as well. We note in passing that these results may also be applicable to polytypes. The choice of polytype of a growing crystal depends on factors including the presence of impurities. Vodakov *et al.* [10] and Stein and Lanig [11] discuss this for the polytypic material SiC as do Jain and Trigunayat [12] and Salje *et al.* [13] for the polytypic material PbI_2. In the application of this model to oscillatory zoning we write a free energy functional of strain coordinates and consider how allowing composition variations modifies it. To apply the model to polytypism one would have to write a free energy functional in terms of an order parameter and consider how compositional variations would alter the form of the functional.

2 A one-dimensional system with an oscillating surface relaxation

A surface relaxation is a strain field, which decays from a non-zero value at the surface of a crystal to zero in the bulk of the crystal. The bulk configuration is taken as the reference state for strains. Physically the origin of a surface relaxation lies in the fact that atoms in surface layers are not in the same environment as atoms in bulk layers. Therefore the configuration of surface atoms that minimises the free energy of the crystal is not the same as the ideal configuration of atoms in the bulk layers. Long range interactions between atoms insure that the strains generated at the surface affect other layers. Without these long range interactions the relaxation would be restricted to the surface layers.

To produce an oscillatory surface relaxation in a model of a crystal with harmonic interactions between atomic planes requires interactions between 1st, 2nd and 3rd nearest neighbour planes [14]. In a continuum model

---

[a] e-mail: `wlee@esc.cam.ac.uk`

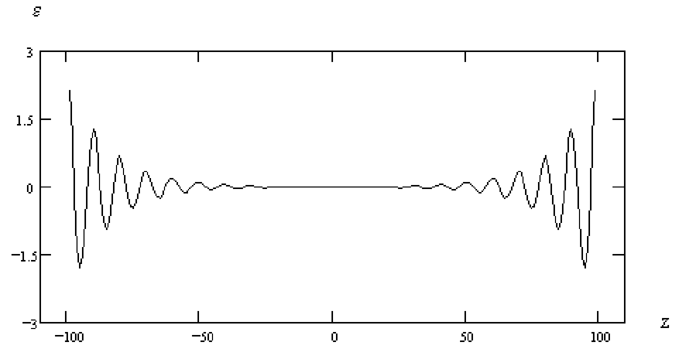

Fig. 1. An oscillatory surface relaxation. The parameters of the above free energy are taken as $a = 1$, $\alpha = 1$, $\beta = 1$, $\lambda = 1.393$, $\mu = 0.995$, $\varepsilon_0 = 1$, $\varepsilon_0' = 1$ see equation (1). λ and μ are chosen to give $K_\mathrm{i} = 0.1$ and $K_\mathrm{r} = 1$ see equation (2).

this gives us a free energy functional of the strain as shown in equation (1).

$$F[\varepsilon] = \int_0^L \left[\frac{a}{2}\varepsilon^2 - \frac{a\lambda^2}{2}\left(\frac{\partial\varepsilon}{\partial z}\right)^2 + \frac{a\mu^4}{2}\left(\frac{\partial^2\varepsilon}{\partial z^2}\right)^2\right]\mathrm{d}z + \left[\frac{\alpha}{2}(\varepsilon-\varepsilon_0)^2 + \frac{\beta}{2}\left(\frac{\partial\varepsilon}{\partial z} - \varepsilon_0'\right)^2\right]_{z=L}. \tag{1}$$

There is a bulk term and a surface term. The system is symmetrical about $z = 0$: there is another surface at $z = -L$. The ideal surface strain and gradient in the strain are non-zero whereas in the bulk ideally the strain is zero. The strain relaxes from its surface values to its bulk value (zero) in an oscillatory manner. Figure 1 shows the strain profile of an oscillatory surface relaxation. The oscillation has wavenumber K_i and the exponential decay has decay constant K_r. In terms of these two constants, λ and μ are given by:

$$\lambda = \left[\frac{2(K_\mathrm{i}^2 - K_\mathrm{r}^2)}{(K_\mathrm{i}^2 + K_\mathrm{r}^2)^2}\right]^{\frac{1}{2}}$$
$$\mu = \frac{1}{(K_\mathrm{i}^2 + K_\mathrm{r}^2)^{1/2}}\,. \tag{2}$$

Obviously a system with such a free energy functional will be unstable if λ is too large. We can calculate a stability condition on λ by considering the bulk free energy per unit length

$$f = \frac{a}{2}\varepsilon^2 - \frac{a\lambda^2}{2}\left(\frac{\partial\varepsilon}{\partial z}\right)^2 + \frac{a\mu^4}{2}\left(\frac{\partial^2\varepsilon}{\partial z^2}\right)^2. \tag{3}$$

For the system to be stable against ferroelastic transitions the minimum value of the bulk free energy must occur when $\varepsilon = 0$. Clearly this gives us $f = 0$ also. If the system can lower it's free energy below zero by developing an oscillatory strain then the system will undergo a ferroelastic transition. To determine a stability condition on λ we set $\varepsilon = \ cos(kz)$ in the equation for f and average over a cycle of the oscillations. This gives us f as a function of k, we find the non-zero value of k that minimises f: k_min. If $f(k_\mathrm{min})$ is positive then this is not an absolute minimum, the absolute minimum is $\varepsilon = 0$ and the system is stable. If however $f(k_\mathrm{min})$ is negative then the system is unstable, since it can lower it's free energy by developing an oscillatory strain. These considerations give us the stability condition $\lambda < \sqrt{2}\mu$.

3 Surface relaxations interacting with composition variations

To understand how to incorporate a composition variable ξ into the above free energy consider a substitutional solid solution $\mathrm{A}_n\mathrm{B}_{1-n}$ in contact with a melt or solution. The solid has an ideal composition which we label as $\xi = 0$. This composition must correspond to a minimum in the free energy of the system. A positive ξ means the solid solution contains an excess amount of A, a negative ξ means that the solid solution contains too little A. The relevant free energy contains a term quadratic in ξ with a minimum at $\xi = 0$. A change in composition causes a change in the lattice parameters of the solid solution. To a good approximation this change will be linear in ξ (Vegards law). With the strain variable ε representing deviations from the reference configuration where the lattice parameters are those of the $\xi = 0$ solid solution we have $\varepsilon \propto \xi$. For simplicity we scale ξ so that the constant of proportionality is one. Now the minimum in the elastic strain energy is about $\varepsilon = \xi$ rather than about $\varepsilon = 0$. Incorporating these two features into our free energy functional gives:

$$F[\varepsilon,\xi] = \int_0^L \left[\frac{b}{2}\xi^2 + \frac{a}{2}(\varepsilon-\xi)^2 - \frac{a\lambda^2}{2}\left(\frac{\partial\varepsilon}{\partial z}\right)^2 + \frac{a\mu^4}{2}\left(\frac{\partial^2\varepsilon}{\partial z^2}\right)^2\right]\mathrm{d}z + \left[\frac{\alpha}{2}(\varepsilon-\varepsilon_0)^2 + \frac{\beta}{2}\left(\frac{\partial\varepsilon}{\partial z} - \varepsilon_0'\right)^2\right]_{z=L}. \tag{4}$$

The first term in the integral shows that the minimum in the free energy of the system is $\xi = 0$. The second term shows that altering the composition of the system alters the lattice parameter. If ξ is held equal to zero (or any other constant value) then the stability condition for this system is the same as the previous one. However if ξ is allowed to oscillate at the same frequency as the strain then the stability condition derived in the previous section is weakened to

$$\lambda < \left(\frac{4b}{a+b}\right)^{\frac{1}{4}}\mu.$$

That means that a system that is stable against purely ferroelastic transitions may be unstable against a transition involving both variations in the strain and in composition. This means that for materials of this sort oscillatory crystal zoning represents an equilibrium state rather than the result of growth kinetics.

4 Growth of an oscillatory zoned crystal

Strain relaxations take place at the speed of sound, which can be considered instantaneous on the timescale of crystal growth. Composition relaxation takes place by diffusion, which can be an extremely slow process. Therefore in calculating the strain and composition profiles of a crystal we minimise the free energy functional completely with respect to the strain variable ε but we only allow the composition variable ξ to vary in the surface layers. In the bulk of the material ξ remains fixed. This means we have to calculate the composition profile in a series of steps. In each step the crystal grows (in one dimension) by length δ. The composition profile in the surface layers takes its equilibrium shape. The composition profile in the rest of the crystal remains in the same shape it had in the previous step.

The boundary conditions are

$$\begin{aligned} \alpha\varepsilon - a\lambda^2\frac{\partial\varepsilon}{\partial z} - a\mu^4\frac{\partial^3\varepsilon}{\partial z^3} &= \alpha\varepsilon_0 \\ \beta\frac{\partial\varepsilon}{\partial z} + a\mu^4\frac{\partial^2\varepsilon}{\partial z^2} &= \beta\varepsilon_0'. \end{aligned} \tag{5}$$

The surface layers are characterised by

$$\begin{aligned} \frac{b}{a+b}\varepsilon + \lambda^2\frac{\partial^2\varepsilon}{\partial z^2} + \mu^4\frac{\partial^4\varepsilon}{\partial z^4} &= 0 \\ \xi = \frac{a}{a+b}\varepsilon & \end{aligned} \tag{6}$$

and the bulk layers follow the equation

$$\varepsilon + \lambda^2\frac{\partial^2\varepsilon}{\partial z^2} + \mu^4\frac{\partial^4\varepsilon}{\partial z^4} = \xi. \tag{7}$$

To solve these equations numerically we converted them to finite difference equations. The surface layer was taken to be $2\pi/K_\mathrm{i}$ one wavelength in the purely elastic ($\xi = 0$) oscillatory relaxation *i.e.* K_i is calculated from λ and μ and equation (2). The system was broken up into a grid of size $\delta = 2\pi/10K_\mathrm{i}$. The equations were solved repeatedly as a matrix inversion problem, each time the size of the system was increased by one grid unit. For a sufficiently low value of b the results show oscillations in composition of increasing amplitude. These oscillations grow in amplitude without limit in these simulations because there are no higher order terms *e.g.* $\frac{c}{4}\left(\frac{\partial\varepsilon}{\partial z}\right)^4$ in the free energy functional to prevent them from growing indefinitely. In a real crystal the oscillations would saturate at finite amplitude due to such higher order terms. Examples of the composition and strain profiles obtained are given in Figures 2 and 3. Here the parameters are chosen so that the system is stable against purely elastic transitions but unstable against coupled elastic and composition transitions.

5 Conclusions

The above results show that allowing a system with an oscillatory surface relaxation an extra degree of freedom associated with composition variations can make it unstable with respect to a state in which the oscillatory relaxation propagates through the bulk of the crystal, pinned in place by an oscillating composition. This is clearly an example of oscillatory zoning, with a sinusoidal variation in impurity concentration. Unlike many of the models of oscillatory zoning the oscillating composition is an equilibrium state rather than the result of non-equilibrium growth.

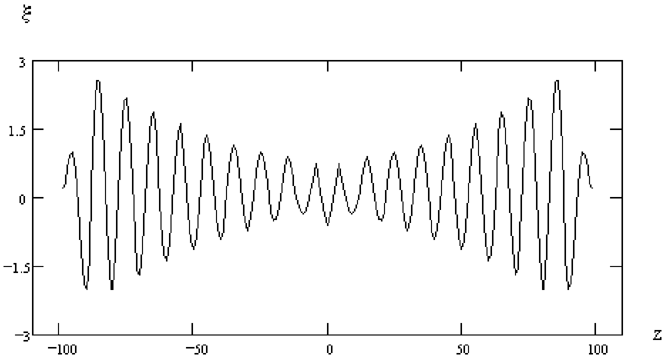

Fig. 2. Variation in composition across a growing crystal. The composition is free to vary in the surface layers but is fixed in the bulk while the crystal is grown. Higher order terms in the free energy will cause these oscillations to saturate out at some finite amplitude. This is an example of composition variations driving a crystal through a ferroelastic phase transition. The parameters of the free energy functional, equation (4), are $a = 1$, $b = 10$, $\alpha = 1$, $\beta = 1$, $\varepsilon_0 = 1$, $\varepsilon_0' = 1$, $\lambda = 1.393$, $\mu = 0.995$.

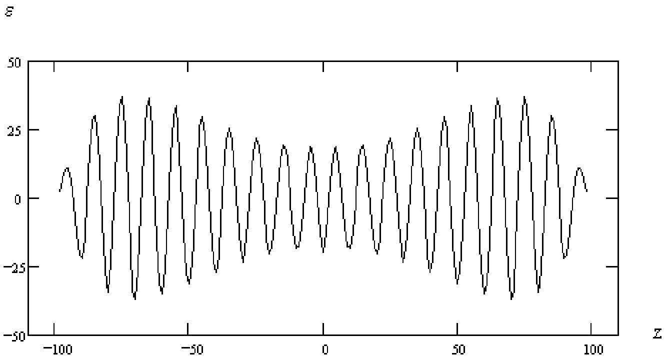

Fig. 3. Strain profile produced by the defect concentration profile shown in Figure 2.

W.T.L thanks NERC for funding his studentship.

References

1. M. Shore, A.D. Fowler, Can. Mineral. **34**, 1111-1126 (1996).
2. A. Putnis, L. Fernandez-Diaz, M. Prieto, Nature **358**, 743-745 (1992).

3. D.R. Wones, in *The evolution of igneous rocks: fiftieth anniversary Perspectives*, edited by H.S. Yoder (Princeton university press, Princeton, New Jersey 1979).
4. J. Phemister, Mineralogical Mag. **23**, 541-555 (1934).
5. W.J. Meyers, J. Sediment. Petrol. **44**, 837-861 (1974).
6. W.J. Meyers, Sedimentology **25**, 371-400 (1978).
7. Y. Wang, E. Merino, Geochim. Cosmochim. Acta **56**, 587-596 (1992).
8. T.H. Pearce, in *Feldspars and their reactions*, edited by I. Parson (Kluwer Academic Publishers, London 1994).
9. W.T. Lee, E.K.H. Salje, M.T. Dove, J. Phys. Cond. Matter **11**, 7385-7410 (1999).
10. Yu A. Vodakov, E.N. Mokhov, A.D. Roenkov, Phys. Stat. Sol. A **51**, 209-215 (1979).
11. R.A. Stein, P. Lanig, J. Cryst. Growth **131**, 71-74 (1993).
12. A. Jain, G.C. Trigunayat, Acta Cryst. A **52**, 590-595 (1996).
13. E.K.H. Salje, B. Palosz, B. Wruck, J. Phys. C **20**, 4077-4096 (1987).
14. B. Houchmandzadeh, J. Lajzerowicz, E. Salje, J. Phys. Cond. Matter **4**, 9779-9794 (1992).