Chapter 6

Suppression of convection using gradient magnetic fields during crystal growth of $NiSO_4{\cdot}6H_20$

A magnetic field was successfully used to suppress buoyancy driven convection during solution growth of a $NiSO_4{\cdot}6H_2O$ crystal. The disappearance of the convection plume and the expansion of the depletion zones, typical for crystal growth in the absence of gravity, were observed with schlieren microscopy when the product of magnetic field and field gradient corresponds to the condition that for all relevant concentrations buoyancy is compensated by paramagnetic counterforces. We show both theoretically and experimentally, that levitation of the growth solution is not the correct condition to suppress convection.

6.1 Introduction

For a wide variety of technical and scientific applications, the availability of high quality single crystals is of primary importance. For example in protein structure determination with X-ray diffraction, the crystal quality is often the limiting factor. Crystal quality is largely determined by processes during growth. To nucleate crystals from solution, highly supersaturated solutions are needed. Once crystals have nucleated, their growth depletes the solution in the vicinity of the crystal, resulting in a lower local density. This solution will rise due to buoyancy, which leads to convection that can be observed as a so-called growth plume[1]. Through a relatively thin (typically 0.1-0.3 mm) laminar flow boundary layer near the crystal surface, the crystal remains in contact with a highly supersaturated solution. Within this boundary layer, diffusion is the only means of mass-transport, leading to a thin depletion zone with a high concentration gradient. In a system where mass transport is important, this leads to a fast growth rate which affects crystal quality negatively, because defects have no time to heal. Therefore microgravity conditions, which suppress buoyancy, are believed to improve crystal quality, since without convection the depletion zone will extend continuously and crystal growth is automatically slowed down due to much slower mass transport[2].

A second effect that reduces the crystal quality arises from microcrystals that form at high supersaturations. Sedimentation of such microcrystals occurs in normal gravity and leads to increased mosaicity in the crystal after incorporation[3]. In this case microgravity conditions should also improve crystal quality. Therefore crystal growers and protein crystallographers in particular, have performed several growth experiments in space. However, space based experiments are rare and expensive, and have a low controllability and accessibility. The outcome of these studies on the beneficial effect of microgravity on crystal quality is therefore not conclusive[4–6].

6.2 Magnetic fields and convection

A promising alternative for space based experiments is the application of magnetic fields[7]. By applying a gradient magnetic field, a magnetic force is generated which can counteract gravity[8, 9]. Although many crystal growth experiments have been performed in magnetic fields, no experiment has yet shown that simulated microgravity in magnetic fields indeed leads to suppression of convection. In this paper we directly show by schlieren microscopy how the growth plume during crystal growth can be suppressed in a suitably chosen magnetic field.

Following a recent analysis of Ramachandran and Leslie[10] we first briefly discuss the forces acting on a body in a magnetic field. The net force F_z per unit volume along the z-direction on an object in a gradient magnetic field in vacuum or air is the sum of the magnetic force and the gravitational force given by[9, 10]

$$F_z = F_{magnetic} + F_{gravity} = \frac{\chi}{\mu_0} B_z B_z^{'} - \rho g \ , \tag{6.1}$$

with $B_z^{'} = dB_z/dx$, χ the volume magnetic susceptibility, ρ the density, μ_0 the magnetic permeability of the vacuum, g the gravitational acceleration in the $-z$ direction and B_z the magnetic field along the z-direction. To achieve levitation, the magnetic and gravitational force should cancel each other so that $F_z = 0$, from which the levitation condition directly follows and which is demonstrated in levitating diamagnetic materials like bismuth[11], droplets of ionic solution[12], glass[12] and even frogs[9]. However, to obtain a microgravity-like condition for crystal growth where buoyancy driven convection is suppressed, levitation is not the correct condition. During crystal growth from solution, local variations in concentration occur, and thus also local variations in density and magnetic susceptibility. To achieve suppression of convection the force acting on different volume elements of the growth solution should be equal, leading to the following condition:

$$B_z B_z^{'} = \frac{\Delta\rho}{\Delta\chi} \mu_0 g \ , \tag{6.2}$$

with $\Delta\rho$ and $\Delta\chi$ the difference in the density and the volume magnetic susceptibility respectively between different solutal volume elements. For small variations in the concentration the density and susceptibility can be written as $\rho(c) = \alpha c + \rho_0$ and $\chi(c) = \beta c + \chi_0$, with α and β the coefficients of the linear concentration dependence of ρ and χ respectively. Eqn. (6.2) then becomes

$$B_z B_z^{'} = \frac{\alpha}{\beta}\mu_0 g \ . \tag{6.3}$$

α is usually positive, while for diamagnetic materials χ is negative and of the order of 10^{-6}, with β usually also negative and small. Therefore, $B_z B_z^{'}$ has to have a large and negative value, mostly beyond the reach of conventional magnets. For paramagnetic solutions, β is positive and much larger, which makes suppression of convection more easy. Note that Eqn. 6.2 and 6.3 show that if $\beta = 0$ it is impossible to suppress buoyancy driven convection, although it is possible to levitate the solution[13, 14].

Another consequence of the previous analysis is that the criterion to reduce sedimentation is given by Eqn. 6.2, which has been used by Maki *et al.* to grow lysozyme crystals floating in a paramagnetic solution[15]. Unlike in real microgravity, suppression of convection, reducing sedimentation or levitation cannot be done simultaneously using gradient magnetic fields.

6.3 Experimental setup

For an experimental validation of this method for convection suppression during growth, we investigated the growth of $NiSO_4 \cdot 6H_2O$ crystals from solution in a gradient magnetic field. Nickel sulfate crystals and their solution are paramagnetic. In order to calculate the conditions for convection suppression we measured the density and volume susceptibility as function of concentration range near the equilibrium concentration of 48.88 wt% at 25 ^{o}C[16]. The density measurements were performed by weighing a precisely determined volume of solution. The volume susceptibility measurements were performed using a MSB-Auto magnetic susceptibility balance from Sherwood Scientific Ltd. Results for these measurements are shown in Figure 6.1. We determined the

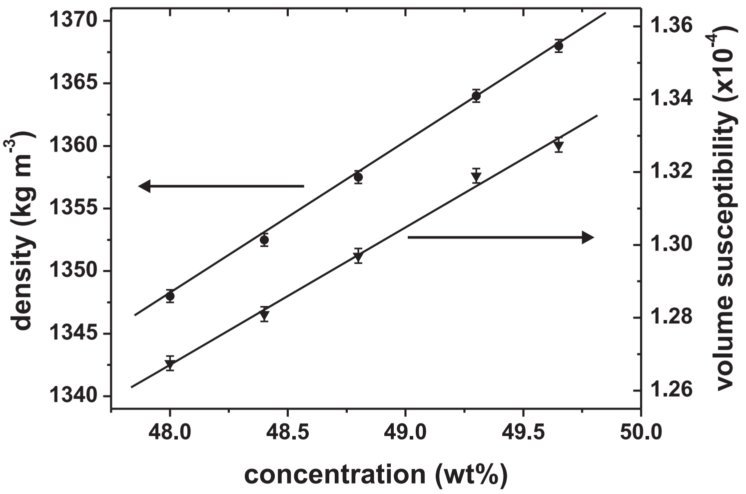

Figure 6.1: Density and susceptibility as function of concentration of an aqueous $NiSO_4 \cdot 6H_2O$ solution.

following values:

- α=12.1±0.5 kg m^{-3} wt% $^{-1}$
- β=(3.8±0.2)×10^{-6} wt% $^{-1}$

6.4 Results and Discussion

With all parameter values known, we can calculate the required $B_z B_z^{'}$ to suppress convection, stop sedimentation or to levitate the solution. We have estimated χ_{crystal} to be 3.2×10^{-4} by extrapolation of the data in figure 6.1. The values are shown in table 6.1, which also shows the predicted effective g value for convection.

Our experiments were performed using a 20 Tesla 32 mm bore resistive magnet with a calibrated field profile at the High Field Magnet Laboratory at the Radboud University Nijmegen. The position in the magnet we chose to perform our experiment has values of $B_z = 0.434 B_0$ and $B_z^{'} = 14.555 B_z$, where B_0 is the maximum field at the center of the magnet. The samples were prepared by gluing small single crystal fragments to a thin copper wire using superglue. These crystals were submerged in a slightly supersaturated solution so that they grew to a size of about 1 mm. The crystals were mounted in a glass cuvette with an inner volume of 7.5x7.5x15 mm^3. A long distance schlieren-type microscope was built to fit inside the magnet bore. With schlieren microscopy it is possible to visualize concentration gradients in-situ because the intensity is proportional to the gradient in concentration along the x-direction, i.e., $I \propto \partial n/\partial x \propto \partial c/\partial x$[17–19]. The temperature inside the bore was set to 25 ^{o}C and controlled by a double-walled tube connected to a thermostatic water bath. As growth solution, a 10.5% supersaturated nickel sulfate hexahydrate solution was used.

Figure 6.2 shows the main result of our experiment. At $B_z = 0T$, under normal gravity conditions, a growth plume can be seen rising from the crystal (Fig. 6.2a). At the sides of the crystal, zones of low and high intensities are visible. These are the depletion zones surrounding the crystal. The concentration gradient on the left side of the crystal is positive and on the right side of the crystal negative, leading to higher and lower intensities because of the schlieren principle. The average width of this depletion zone in the x-direction is 0.25 mm, which is a normal value. When slowly sweeping the field, we found that the growth plume disappeared for $B_z = 1.6T$. At this point, an effective microgravity condition was obtained with complete suppression of convection. After a transient of a few seconds due to the disappearance of the plume, the expansion of the depletion zones around the crystal took several minutes until the depleted zone reached a more or less fixed width of about 1 mm, 4 times as wide as at normal gravity conditions (fig. 6.2b).

Table 6.1 shows that the experimental value for $B_z B_z^{'}$ as calculated from the field profile, agrees well with the predicted one from α and β. From this we can conclude that linearization of $\rho(c)$and $\chi(c)$ is a valid approximation.

Increasing $B_z B_z^{'}$ creates an inverse effective gravity. In figure 6.2c, a schlieren image is shown of the same growing crystal, but now with the growth plume directed downwards. The applied field was $B_z = 3.5T$. The width of the depletion zones decreased to approximately 0.25 mm again. We observed a

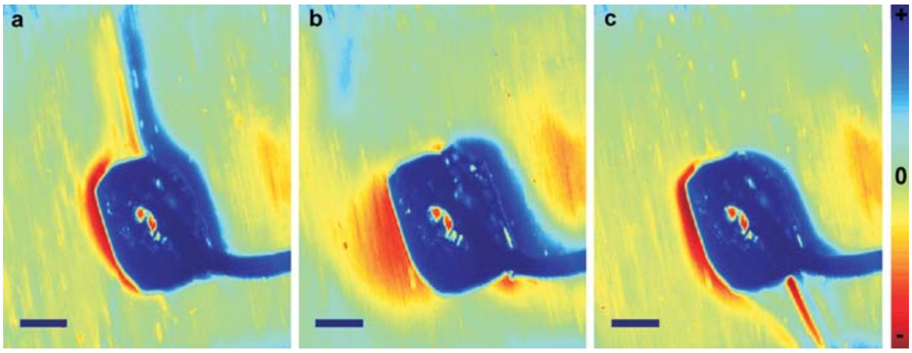

Figure 6.2: False color schlieren images of growing nickel sulfate crystals. (a) B_z=0 T (normal gravity). The crystal is solid blue and the blue stripe on the bottom-right is the copper wire on which the crystal is fixed. The plume is vertical, but the camera was slightly tilted. (b) After 5 minutes at B_z=1.6 T (suppression of convection) with an expanded depletion zone. (c) B_z=3.5 T (inverse effective gravity). The color indicates the concentration gradient, with red a large negative and blue a large positive gradient, according to the color bar on the right. The scale bar corresponds to 0.5 mm.

Table 6.1: The conditions to achieve suppression of convection, no sedimentation, or levitation.

Condition	B_zB_z' (T^2 m^{-1}) Predicted	B_zB_z' (T^2 m^{-1}) Experimental	$g_{\text{effective}}$ (m s^{-2})
No field	0		1g
Suppression of convection	39±3	37.5±0.5	0g
No sedimentation	45±5		-0.1g
Levitation	123±3		-2g

similar situation for all values of $B_z B_z'$ well above the convection suppression. Thus for the condition of magnetic levitation, convection is strong, and even enhanced as compared to normal gravity (see table 6.1).

In summary, we have reported for the first time that solutal convection during crystal growth can be suppressed by gradient magnetic fields, mimicking microgravity. We have found that the balance between magnetic and gravitational forces can be made sufficiently precise that the depletion zone expands, as expected in the absence of gravity. This leads to a strong reduction in the effective supersaturation, and thus holds promise to yield better crystals. We have proven theoretically as well as experimentally by in-situ schlieren microscopy that levitating the solution is not the right condition to achieve this situation. Some earlier experiments performed under levitation conditions can thus not have achieved convection suppression[13, 14]. Using gradient magnetic fields combined with in-situ optical techniques like schlieren microscopy offers a great opportunity to study the effects of microgravity-like conditions on crystal growth in general and protein crystal growth in particular. Although, unlike in real microgravity, suppression of convection and reducing sedimentation cannot occur simultaneously, the use of gradient magnetic fields can offer a good alternative for microgravity experiments in crystal growth.

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